

SEARCH REQUEST FORM**Scientific and Technical Information Center**

Mrs. Adler
 Requester's Full Name: BEN SACKY Examiner #: 73489 Date: 10/20/02
 Art Unit: 1626 Phone Number 305-3889 Serial Number: 101053297
 Mail Box and Bldg/Room Location: CMI 3E11 Results Format Preferred (circle): PAPER DISK E-MAIL

If more than one search is submitted, please prioritize searches in order of need.

- Please provide a detailed statement of the search topic, and describe as specifically as possible the subject matter to be searched.
- Include the elected species or structures, keywords, synonyms, acronyms, and registry numbers, and combine with the concept or utility of the invention. Define any terms that may have a special meaning. Give examples or relevant citations, authors, etc, if known. Please attach a copy of the cover sheet, pertinent claims, and abstract.

Title of Invention: Process for making vitamin E using hydrogen-tris(oxalato)phosphate

Inventors (please provide full names): BONRATH et al.

Earliest Priority Filing Date: _____

For Sequence Searches Only Please include all pertinent information (parent, child, divisional, or issued patent numbers) along with the appropriate serial number.

Process for making (all-rac)- α -tocopherol comprising a reaction mixture comprising trimethylhydroquinone and isophytol or phytol with a catalyst comprising hydrogen-tris(oxalato)phosphate and an organic solvent.

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|------------------------------|------------------|-----------------|-----------------------------------|
| Searcher: | <u>K. Fuller</u> | NA Sequence (#) | ✓ STN _____ |
| Searcher Phone #: | _____ | AA Sequence (#) | Dialog _____ |
| Searcher Location: | _____ | Structure (#) | <u>2</u> Questel/Orbit _____ |
| Date Searcher Picked Up: | _____ | Bibliographic | Dr. Link _____ |
| Date Completed: | <u>10/21/02</u> | Litigation | Lexis/Nexis _____ |
| Searcher Prep & Review Time: | <u>20</u> | Fulltext | Sequence Systems _____ |
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IFIUDB
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ZCAPLUS
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NEWS 12 Jul 02 FOREGE no longer contains STANDARDS file segment
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NEWS 17 Aug 08 PHARMAMarketLetter (PHARMAML) - new on STN
NEWS 18 Aug 08 NTIS has been reloaded and enhanced
NEWS 19 Aug 19 Aquatic Toxicity Information Retrieval (AQUIRE)
now available on STN
NEWS 20 Aug 19 IFIPAT, IFICDB, and IFIUDB have been reloaded
NEWS 21 Aug 19 The MEDLINE file segment of TOXCENTER has been reloaded
NEWS 22 Aug 26 Sequence searching in REGISTRY enhanced
NEWS 23 Sep 03 JAPIO has been reloaded and enhanced
NEWS 24 Sep 16 Experimental properties added to the REGISTRY file
NEWS 25 Sep 16 CA Section Thesaurus available in CAPLUS and CA
NEWS 26 Oct 01 CASREACT Enriched with Reactions from 1907 to 1985
NEWS 27 Oct 21 EVENTLINE has been reloaded
NEWS 28 Oct 24 BEILSTEIN adds new search fields
NEWS 29 Oct 24 Nutraceuticals International (NUTRACEUT) now available on
STN
NEWS 30 Oct 25 MEDLINE SDI run of October 8, 2002
NEWS 31 Nov 18 DKILIT has been renamed APOLLIT
NEWS 32 Nov 25 More calculated properties added to REGISTRY
NEWS 33 Dec 02 TIBKAT will be removed from STN
NEWS 34 Dec 04 CSA files on STN
NEWS 35 Dec 17 PCTFULL now covers WP/PCT Applications from 1978 to date
NEWS 36 Dec 17 TOXCENTER enhanced with additional content
NEWS 37 Dec 17 Adis Clinical Trials Insight now available on STN
NEWS 38 Dec 30 ISMEC no longer available

NEWS 39 Jan 13 Indexing added to some pre-1967 records in CA/CAPLUS
NEWS 40 Jan 21 NUTRACEUT offering one free connect hour in February 2003
NEWS 41 Jan 21 PHARMAML offering one free connect hour in February 2003
NEWS 42 Jan 29 Simultaneous left and right truncation added to COMPENDEX,
ENERGY, INSPEC
NEWS 43 Feb 13 CANCERLIT is no longer being updated
NEWS 44 Feb 24 METADEX enhancements
NEWS 45 Feb 24 PCTGEN now available on STN
NEWS 46 Feb 24 TEMA now available on STN

NEWS EXPRESS January 6 CURRENT WINDOWS VERSION IS V6.01a,
CURRENT MACINTOSH VERSION IS V6.0b(ENG) AND V6.0Jb(JP),
AND CURRENT DISCOVER FILE IS DATED 01 OCTOBER 2002

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Property values tagged with IC are from the ZIC/VINITI data file provided by InfoChem.

STRUCTURE FILE UPDATES: 24 FEB 2003 HIGHEST RN 494745-03-8
DICTIONARY FILE UPDATES: 24 FEB 2003 HIGHEST RN 494745-03-8

TSCA INFORMATION NOW CURRENT THROUGH MAY 20, 2003

Please note that search-term pricing does apply when conducting SmartSELECT searches.

Crossover limits have been increased. See HELP CROSSOVER for details.

Experimental and calculated property data are now available. See HELP PROPERTIES for more information. See STNote 27, Searching Properties in the CAS Registry File, for complete details:
<http://www.cas.org/ONLINE/STN/STNOTES/stnotes27.pdf>

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=> s 174749-62-3/rn
L1      1 174749-62-3/RN
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=> d 11 all
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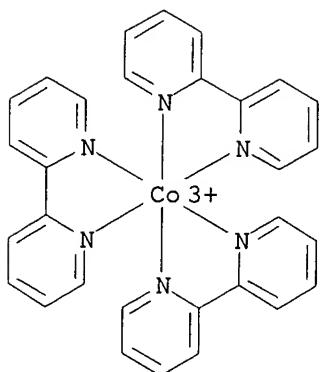
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L1  ANSWER 1 OF 1  REGISTRY  COPYRIGHT 2003 ACS
RN  174749-62-3  REGISTRY
CN  Cobalt(3+), tris(2,2'-bipyridine-N,N')-, (OC-6-11)-, sodium
    hexafluorophosphate(1-) (OC-6-11)-tris[ethanedioato(2)-O,O']chromate(3-)
    (1:1:1:1) (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN  Chromate(3-), tris[ethanedioato(2)-O,O']-, (OC-6-11)-, sodium
    (OC-6-11)-tris(2,2'-bipyridine-N,N')cobalt(3+) hexafluorophosphate(1-)
    (1:1:1:1) (9CI)
OTHER NAMES:
CN  Tris(2,2'-bipyridine)cobalt(3+) tris(oxalato)chromate(3-) sodium
    hexafluorophosphate(1-)
MF  C30 H24 Co N6 . C6 Cr O12 . F6 P . Na
SR  CA
LC  STN Files:  CA, CAPLUS
```

Ring System Data

| Elemental Analysis | Elemental Sequence | Size of the Rings | Ring System Formula | Identifier | Ring RID | Occurrence Count |
|--------------------|--------------------|-------------------|---------------------|------------|----------|------------------|
| EA | ES | SZ | RF | RID | | |
| C2CrO2- | CrOC2O- | 5-5-5 | C6CrO6 | 1523.80.1 | 1 in CM | |
| C2CrO2-C2CrO2 | CrOC2O-CrOC2O | | | | 3 | |
| C2CoN2- | CoNC2N- | 5-5-5-6-6-6- | C30CoN6 | 13130.7.1 | 1 in CM | |
| C2CoN2- | CoNC2N- | 6-6-6 | | | 1 | |
| C2CoN2-C5N- | ConC2N-NC5- | | | | | |
| C5N-C5N-C5N- | NC5-NC5-NC5- | | | | | |
| C5N-C5N | NC5-NC5 | | | | | |

CM 1

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CRN  19052-39-2
CMF  C30 H24 Co N6
CCI  CCS
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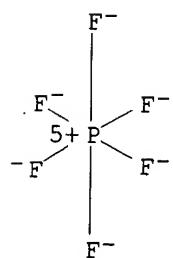


CM 2

CRN 16919-18-9

CMF F6 P

CCI CCS

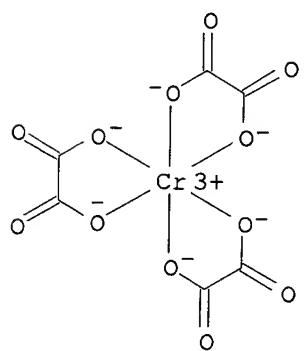


CM 3

CRN 15054-01-0

CMF C6 Cr 012

CCI CCS



1 REFERENCES IN FILE CA (1962 TO DATE)
1 REFERENCES IN FILE CAPLUS (1962 TO DATE)

REFERENCE 1

AN 124:248655 CA
TI Chiral, Three-Dimensional Supramolecular Compounds: Homo- and Bimetallic Oxalate- and 1,2-Dithiooxalate-Bridged Networks. A Structural and Photophysical Study
AU Decurtins, Silvio; Schmalle, Helmut W.; Pellaux, Rene; Schneuwly, Philippe; Hauser, Andreas
CS Institut fuer Anorganische Chemie, Universitaet Zuerich, Zurich, CH-8057, Switz.
SO Inorganic Chemistry (1996), 35(6), 1451-60
CODEN: INOCAJ; ISSN: 0020-1669
PB American Chemical Society
DT Journal
LA English
CC 78-7 (Inorganic Chemicals and Reactions)
Section cross-reference(s): 73, 75
AB In analogy to the [MII(bpy)3]2+ cations (MII = transition-metal; bpy = 2,2'-bipyridine), [MIII(bpy)3]3+ cations (MIII = Cr or Co) induce the crystn. of chiral, anionic three-dimensional (3D) coordination polymers of oxalate-bridged (.mu.-ox) metal complexes [MII2(ox)3]n2n- or [MIMIII(ox)3]n2n-. The tripos. charge is partially compensated by inclusion of addnl. complex anions like ClO4-, BF4-, or PF6- which are encapsulated in cubic shaped cavities formed by the bipyridine ligands of the cations. Thus, an elaborate structure of cationic and anionic species within a polymeric anionic network is realized. The compds. isolated and structurally characterized include [Cr(bpy)3][ClO4] [NaCr(ox)3] (1), [Cr(bpy)3][ClO4][Mn2(ox)3] (2), [Cr(bpy)3][BF4][Mn2(ox)3] (3), [Co(bpy)3][PF6][NaCr(ox)3] (4). Crystal data: 1, cubic, space group P213, a 15.523(4) .ANG., Z = 4; 2, cubic, space group P4132, a 15.564(3) .ANG., Z = 4; 3, cubic, P4132, a 15.553(3) .ANG., Z = 4; 4, cubic, P213, a 15.515(3) .ANG., Z = 4. Also, it seemed likely that 1,2-dithiooxalate (dto) could act as an alternative to the oxalate bridging ligand, and as a result [Ni(phen)3][NaCo(dto)3].cntdot.C3H6O (5) has successfully been isolated and structurally characterized. Crystal data: 5, orthorhombic, space group P212121, a 16.238(4), b 16.225(4), c 18.371(5) .ANG., Z = 4. The photophys. properties of 1 were studied. In single crystal absorption spectra of [Cr(bpy)3][ClO4][NaCr(ox)3] (1), the spin-flip transitions of both the [Cr(bpy)3]3+ and the [Cr(ox)3]3- chromophores are obsd. and can be clearly distinguished. Irradiating into the spin-allowed 4A2 .fwdarw. 4T2 absorption band of [Cr(ox)3]3- results in intense luminescence from the 2E state of [Cr(bpy)3]3+ as a result of rapid energy transfer processes.
ST crystal structure chromium cobalt bipyridine oxalatometalate; bipyridine chromium cobalt oxalatometalate prepn; manganate oxalato chromium cobalt bipyridine prepn; thiooxalato cobaltate nickel phenanthroline prepn structure; photophys chromium bipyridine oxalatochromate; luminescence chromium bipyridine oxalatochromate; absorption spectra chromium

bipyridine oxalatochromate
IT Energy level transition
Energy transfer
Luminescence
Ultraviolet and visible spectra
(of bipyridinechromium oxalatochromate)
IT Crystal structure
Molecular structure
(of chromium/cobalt bipyridine oxalatotransition metalate and chromium phenanthroline dithiooxalatochromate complexes)
IT Imines
RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
(di-, transition metal complexes, oxalatochromate/manganate and dithiooxalatocobaltate; prepn. and crystal structure of)
IT Transition metal compounds
RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
(diimine complexes, oxalatochromate/manganate and dithiooxalatocobaltate; prepn. and crystal structure of)
IT 23539-86-8, Tris(2,2'-bipyridine)chromium(3+) triperchlorate
RL: RCT (Reactant); RACT (Reactant or reagent)
(for prepn. of chromium bipyridine oxalatochromate/manganate complexes)
IT 174749-67-8, Tris(2,2'-bipyridine)chromium(3+)
tris(tetrafluoroborate(1-))
RL: RCT (Reactant); RACT (Reactant or reagent)
(for prepn. of chromium bipyridine oxalatomanganate complexes)
IT 14217-01-7, Tripotassium tris(oxalato)chromate(3-)
RL: RCT (Reactant); RACT (Reactant or reagent)
(for prepn. of chromium/cobalt bipyridine oxalatochromate complexes)
IT 28277-53-4, Tris(2,2'-bipyridine)cobalt(3+) tris(hexafluorophosphate(1-))
RL: RCT (Reactant); RACT (Reactant or reagent)
(for prepn. of cobalt bipyridine oxalatochromate complex)
IT 39016-57-4, Tris(1,10-phenanthroline)nickel(2+) sulfate 92348-93-1
RL: RCT (Reactant); RACT (Reactant or reagent)
(for prepn. of nickel phenanthroline dithiooxalatocobaltate complex)
IT 174749-59-8P, Tris(2,2'-bipyridine)chromium(3+) tris(oxalato)chromate(3-)
sodium perchlorate
RL: PEP (Physical, engineering or chemical process); PRP (Properties);
SPN
(Synthetic preparation); PREP (Preparation); PROC (Process)
(prepn. and crystal structure and photophys. of)
IT 174749-60-1P, Tris(2,2'-bipyridine)chromium(3+)
tris(oxalato)dimanganate(2-)
) perchlorate 174749-62-3P, Tris(2,2'-bipyridine)cobalt(3+)
tris(oxalato)chromate(3-) sodium hexafluorophosphate(1-) 174749-64-5P,
Tris(1,10-phenanthroline)nickel(2+) tris(dithiooxalato)cobaltate(3-)
sodium acetone
RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
(prepn. and crystal structure of)
IT 174749-59-8DP, Tris(2,2'-bipyridine)chromium(3+)
tris(oxalato)chromate(3-)
sodium perchlorate, solid soln. with tris(bipyridine)rhodium analog
174749-66-7DP, Tris(2,2'-bipyridine)rhodium(3+) tris(oxalato)chromate(3-)
sodium perchlorate, solid soln. with tris(bipyridine)chromium analog
RL: PEP (Physical, engineering or chemical process); PRP (Properties);
SPN

(Synthetic preparation); PREP (Preparation); PROC (Process)
(prepn. and luminescence of)
IT 174749-61-2P
RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
(s.c.9; codpn. and crystal structure of)
IT 174749-61-2P
RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
(s.c.9; prepn. and crystal structure of)

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| | SINCE FILE | TOTAL |
|--|------------|---------|
| | ENTRY | SESSION |

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FILE LAST UPDATED: 24 Feb 2003 (20030224/ED)

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> s l1 and chelate

1 L1

39189 CHELATE

L2 0 L1 AND CHELATE

=> s l1 and catalyst

1 L1

614401 CATALYST

L3 0 L1 AND CATALYST

=> s l1 and organic synthesis

1 L1

286892 ORGANIC

1044916 SYNTHESIS

7826 ORGANIC SYNTHESIS
(ORGANIC(W) SYNTHESIS)
L4 0 L1 AND ORGANIC SYNTHESIS

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| CA SUBSCRIBER PRICE | 0.00 | -0.62 |

STN INTERNATIONAL LOGOFF AT 18:12:00 ON 25 FEB 2003

=> s ?tocopherol?(L)?hydroquinon?(1)?phytol?(1)phospha?
26251 ?TOCOPHEROL?
48390 ?HYDROQUINON?
3511 ?PHYTOL?
696077 PHOSPHA?
L1 4 ?TOCOPHEROL?(L)?HYDROQUINON?(L)?PHYTOL?(L)PHOSPHA?

=> d bib hit 1-4

L1 ANSWER 1 OF 4 CAPLUS COPYRIGHT 2003 ACS
AN 2002:930649 CAPLUS
TI Final Report on the Safety Assessment of Tocopherol, Tocopheryl Acetate, Tocopheryl Linoleate, Tocopheryl Linoleate/Oleate, Tocopheryl Nicotinate, Tocopheryl Succinate, Dioleyl Tocopheryl Methylsilanol, Potassium Ascorbyl Tocopheryl Phosphate, and Tocopersolan
AU Fiume, Monice Zondlo
CS NW, 1101 17th Street, Cosmetic Ingredient Review, Suite 310, Washington, DC, 20036, USA
SO International Journal of Toxicology (2002), 21(6), 51-116
CODEN: IJTOFN; ISSN: 1091-5818
PB Taylor & Francis Ltd.
DT Journal
LA English
AB **Tocopherol** and its several ester and ether derivs. all function as antioxidants in cosmetic formulations; they also have other functions, such as skin conditioning. Tocopheryl Acetate, **Tocopherol**, and Tocopheryl Linoleate are used in 2673 formulations, generally at concns. of up to 36, 5, and 2, resp., although Tocopheryl Acetate is 100 of vitamin E oil. Tocopersolan, Tocopheryl Linoleate/Oleate, Tocopheryl Nicotinate, Tocopheryl Succinate, Dioleyl Tocopheryl Methylsilanol, and Potassium Ascorbyl Tocopheryl **Phosphate**, combined, are used in 36 formulations at concns. lower than those reported for the frequently used ingredients. **Tocopherol** may be isolated from vegetable oils or synthesized using **isophytol** and **methylhydroquinone**. **Tocopherol**, Tocopheryl Acetate, Tocopheryl Linoleate, and Tocopheryl Succinate all were absorbed in human skin. In rat skin, Tocopheryl Acetate is hydrolyzed to **Tocopherol**. **Tocopherol** is a natural component of cell membranes thought to protect against oxidative damage. **Tocopherol**, Tocopheryl Acetate, and Tocopheryl Succinate each were reported to protect against UV radiation- induced skin damage. These ingredients are generally not toxic in animal feeding studies, although very high doses (.gtoreq.2 g/kg/day) have hemorrhagic activity. These ingredients are generally not irritating or sensitizing to skin or irritating to eyes, although a Tocopheryl Acetate did produce sensitization in one animal test, and Tocopersolan was a slight eye irritant in an animal test. Reproductive and developmental toxicity tests in animals using **Tocopherol**, Tocopheryl Acetate, Tocopheryl Succinate, and Tocopersolan were all neg. or showed some effect of reducing toxicity. **Tocopherol**, Tocopheryl Acetate, Tocopheryl Succinate, and Dioleyl Tocopheryl Methylsilanol were almost uniformly neg. These ingredients exhibit antimutagenic activity consistent with their antioxidant properties. **Tocopherol** was not carcinogenic. The ability of **Tocopherol**, Tocopheryl Acetate, and Tocopheryl Succinate to modulate the carcinogenic effect of other agents (e.g., tumor promotion) has been extensively studied. One study showing tumor promotion in mice may be discounted as not reproducible and not consistent with the large vol. of data suggesting that the antioxidant properties of these agents protect against tumor induction. Specifically, the frequent use of **Tocopherol** as a neg. control in other tumor promotion studies suggests that **Tocopherol** is not a tumor promoter. **Tocopherol** has been shown to reduce the photocarcinogenic effect

of UV radiation in mice. Similar studies with Tocopheryl Acetate and Tocopheryl Succinate, however, demonstrated some enhancement of photocarcinogenesis, although the effect was not dose related. In clin. studies, **Tocopherol**, Tocopheryl Acetate, and Tocopheryl Nicotinate were not irritants or sensitizers. A report of a large no. of pos. patch-tests to Tocopheryl Linoleate in one cosmetic product were considered to result from a contaminant or metabolite. The Cosmetic Ingredient Review Expert Panel considered that these data provide an adequate basis on which to conclude that **Tocopherol**, Tocophersolan, Tocopheryl Acetate, Tocopheryl Linoleate, Tocopheryl Linoleate/Oleate, Tocopheryl Nicotinate, Tocopheryl Succinate, Dioleyl Tocopheryl Methylsilanol, and Potassium Ascorbyl Tocopheryl Phosphate are safe as used in cosmetic formulations. Although there were no inhalation toxicity data, these ingredients are used at such low concns. in hair sprays that no inhalation toxicity risk was considered likely. Because **methylhydroquinone** is used in the chem. synthesis of **Tocopherol**, there was concern that **hydroquinone** may be present as an impurity. In such cases, residual levels of **hydroquinone** would be expected to be limited to those achieved by good manufg. practices.

L1 ANSWER 2 OF 4 CAPLUS COPYRIGHT 2003 ACS
AN 2002:573361 CAPLUS.
DN 137:125303
TI Manufacture of (all-rac)-.alpha.-tocopherol
IN Bonrath, Werner; Netscher, Thomas; Wietelmann, Ulrich
PA Roche Vitamins A.-G., Switz.
SO Eur. Pat. Appl., 11 pp.
CODEN: EPXXDW
DT Patent
LA English
FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|--|------|----------|-----------------|----------|
| PI | EP 1227089 | A1 | 20020731 | EP 2002-764 | 20020114 |
| | R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR | | | | |
| | JP 2002284776 | A2 | 20021003 | JP 2002-5681 | 20020115 |
| | CN 1365977 | A | 20020828 | CN 2002-102027 | 20020117 |
| | US 2002161247 | A1 | 20021031 | US 2002-53297 | 20020117 |
| PRAI | EP 2001-101026 | A | 20010118 | | |
| OS | CASREACT 137:125303 | | | | |

RE.CNT 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

AB A process for the manuf. of (.-+.-)-.alpha.-tocopherol by the catalyzed reaction of **trimethylhydroquinone** with **isophytol** or **phytol** is characterized by carrying out the reaction in the presence of hydrogen tris(oxalato)phosphate, or an adduct thereof with a solvent, as the catalyst in an org. solvent. The product of the process is the most active and industrially most important member of the vitamin E group.

L1 ANSWER 3 OF 4 CAPLUS COPYRIGHT 2003 ACS
AN 1968:510116 CAPLUS
DN 69:110116
TI Monolayers of some biologically important quinones
AU Gaines, George L., Jr.
CS Gen. Elec. Res. and Develop. Center, Schenectady, NY, USA
SO Journal of Colloid and Interface Science (1968), 28(2), 331-3
CODEN: JCISA5; ISSN: 0021-9797
DT Journal
LA English
AB Monolayers of ubiquinone 6 (I) and .alpha.-tocopherolquinone

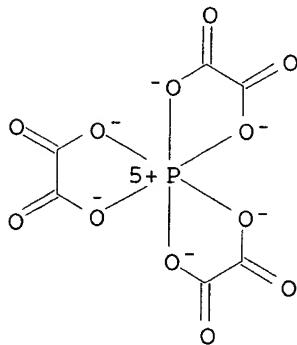
(II) were spread from C₆H₆ solns. on 10-3M phosphate buffer (pH 8) solns. in dim light or darkness. The surface pressure-area curves of I and II are compared with those of vitamin K₁ and phytol. The area requirement in the monolayers is very nearly the same for vitamin K₁ and phytol; the substitution of the bulky naphthoquinone ring for a single hydroxyl group has little effect on the mol. area in these expanded films. In II, the presence of both the quinone and hydroxyl function in each mol. nearly doubles the area occupied, as well as making the film more stable to collapse. The surface potentials due to phytol, vitamin K₁, and II are similar, rising from .apprx.200 to .apprx.250 mv. on compression. I has an unsatd. chain, half again as long as the chain of the other compds. This longer chain, at low surface pressure, permits a greater area per mol. in the expanded film. On compression, however, the I monolayer can be compressed to nearly as small areas as vitamin K₁. The surface potential of a I film ranges from .apprx.350 to >400 mv. on compression. Attempts to demonstrate the redn. of the quinones to the corresponding hydroquinones in the films on aq. subphases were unsuccessful.

L1 ANSWER 4 OF 4 CAPLUS COPYRIGHT 2003 ACS
 AN 1959:105575 CAPLUS
 DN 53:105575
 OREF 53:18965f-i,18966a
 TI .alpha.-Tocopherol esters
 PA E. Merck Chemische Fabrik.
 DT Patent
 LA Unavailable
 FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|----|---|------|----------|-----------------|------|
| PI | GB 811895 | | 19590415 | GB | |
| AB | <p>The diethylaminoacetate of .alpha.-tocopherol was prep'd. as follows: Moist 4,2,3,6-HOME₃C₆HN₂Cl (200 g.) was added to 300 g. ClCH₂CO₂H in 600 ml. of C₆H₆ during 2 hrs. with heating and stirring. The C₆H₆ and excess ClCH₂CO₂H were removed by distn. at 60 mm. and the residue taken up in Et₂O was washed with 1% NH₃ until neutral, dried, filtered and the solvent removed by distn. The residue was stirred with low-boiling petr. ether and the crystals of trimethylhydroquinone which result were filtered off. After evapn. of the mother liquor, distn. of the residue at 1.5 mm. of Hg gave 2,5,6-trimethylhydroquinone chloroacetate (I), m. 116-17.degree.. To 48 g. I in 200 ml. C₆H₆, 30 g. phytol or isophytol and 30 g. ZnCl₂ were added. The mixt. was heated and stirred 5 hrs. in a CO₂ atm. The soln. was washed with H₂O, bleached, and the solvent removed. To sep. unreacted chloroacetate, 60 ml. petr. ether was added. Removal of the solvent and distn. at 219-30.degree. 0.01 mm. gave .alpha.-tocopherol chloroacetate (II) as a greenish yellow oil which crystd. on standing. A mixt. of II, 15 ml. Et₂NH, and 2.5 g. Na₂CO₃ was refluxed 3 hrs., an addnl. 10 ml. of amine was added and refluxing continued 2 hrs. Et₂O was added, excess NaHCO₃ sepd. by filtration and excess amine removed by washing with aq. AcOH. Evapn. of the solvent gave .alpha.-tocopherol diethylaminoacetate (III), a reddish yellow oil. II was also prep'd. by refluxing a mixt. of 50 g. .alpha.-tocopherol in 200 ml. toluene to which was added 50 g. ClCH₂CO₂H during 12 hrs. in a CO₂ atm. III (5 g.) in 3 ml. abs. EtOH made acid with 2N HCl in alc. gave III.HCl, m. 156-7.degree.. Also prep'd. were: III.HBr m. 170-1.degree.; III tartrate, m. 170.degree. (decompn.); .alpha.-tocopherol dimethylaminoacetate-HCl (IV.HCl), m. 192-3.degree.; IV.HBr, m. 202-3.5.degree.; IV sulfate, sinters 225.degree., decomp. 240.degree.. Prepn. of III citrate, III phosphate, and III sulfate were also reported but no phys. consts. given.</p> | | | | |

need to get referred

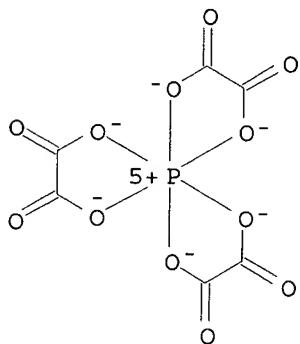
L7 ANSWER 1 OF 4 REGISTRY COPYRIGHT 2003 ACS
 RN 321201-35-8 REGISTRY
 CN Phosphate(1-), tris[ethanedioato(2-)-.kappa.O1,.kappa.O2]-, sodium,
 (OC-6-11)- (9CI) (CA INDEX NAME)
 OTHER NAMES:
 CN Sodium tris(oxalato)phosphate(1-)
 MF C6 O12 P . Na
 CI CCS
 SR CA
 LC STN Files: CA, CAPLUS



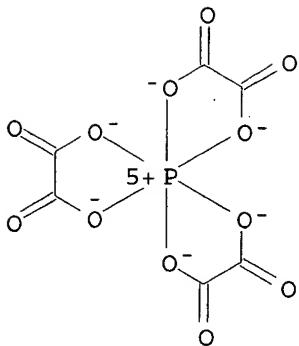
● Na⁺

1 REFERENCES IN FILE CA (1962 TO DATE)
 1 REFERENCES IN FILE CAPLUS (1962 TO DATE)

L7 ANSWER 2 OF 4 REGISTRY COPYRIGHT 2003 ACS
 RN 321201-34-7 REGISTRY
 CN Phosphate(1-), tris[ethanedioato(2-)-.kappa.O1,.kappa.O2]-, hydrogen,
 (OC-6-11)- (9CI) (CA INDEX NAME)
 OTHER NAMES:
 CN Hydrogen tris(oxalato)phosphate(1-)
 MF C6 O12 P . H
 CI CCS
 SR CA
 LC STN Files: CA, CAPLUS, CASREACT, USPATFULL



● H⁺



● H⁺

2 REFERENCES IN FILE CA (1962 TO DATE)
 2 REFERENCES IN FILE CAPLUS (1962 TO DATE)

L7 ANSWER 3 OF 4 REGISTRY COPYRIGHT 2003 ACS

RN 321201-33-6 REGISTRY

CN Phosphate(1-), tris[ethanedioato(2-)-.kappa.O1,.kappa.O2]-, lithium,
 (OC-6-11)- (9CI) (CA INDEX NAME)

OTHER NAMES:

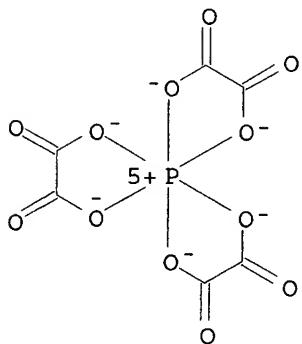
CN Lithium tris(oxalato)phosphate(1-)

MF C6 O12 P . Li

CI CCS

SR CA

LC STN Files: CA, CAPLUS



● Li⁺

1 REFERENCES IN FILE CA (1962 TO DATE)
 1 REFERENCES IN FILE CAPLUS (1962 TO DATE)

~ L7 ANSWER 4 OF 4 REGISTRY COPYRIGHT 2003 ACS

RN 174749-62-3 REGISTRY

CN Cobalt(3+), tris(2,2'-bipyridine-N,N')-, (OC-6-11)-, sodium
 hexafluorophosphate(1-) (OC-6-11)-tris[ethanedioato(2-)-O,O'] chromate(3-)
 (1:1:1:1) (9CI) (CA INDEX NAME)

OTHER CA INDEX NAMES:

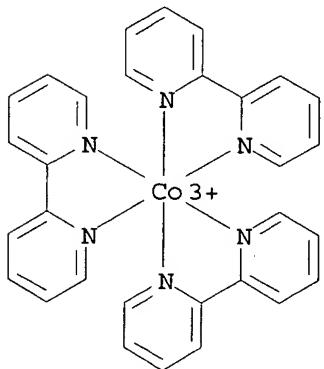
CN Chromate(3-), tris[ethanedioato(2-)-O,O']-, (OC-6-11)-, sodium
 (OC-6-11)-tris(2,2'-bipyridine-N,N') cobalt(3+) hexafluorophosphate(1-)
 (1:1:1:1) (9CI)

OTHER NAMES:

CN Tris(2,2'-bipyridine)cobalt(3+) tris(oxalato)chromate(3-) sodium hexafluorophosphate(1-)
MF C30 H24 Co N6 . C6 Cr O12 . F6 P . Na
SR CA
LC STN Files: CA, CAPLUS

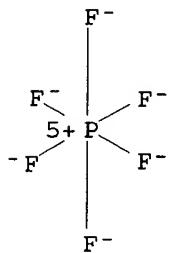
CM 1

CRN 19052-39-2
CMF C30 H24 Co N6
CCI CCS



CM 2

CRN 16919-18-9
CMF F6 P
CCI CCS



CM 3

CRN 15054-01-0
CMF C6 Cr O12
CCI CCS

Crossover limits have been increased. See HELP CROSSOVER for details.

Experimental and calculated property data are now available. See HELP PROPERTIES for more information. See STNote 27, Searching Properties in the CAS Registry File, for complete details:
<http://www.cas.org/ONLINE/STN/STNOTES/stnotes27.pdf>

=> s 174749-62-3/rn
L1 1 174749-62-3/RN

=> d 11 all

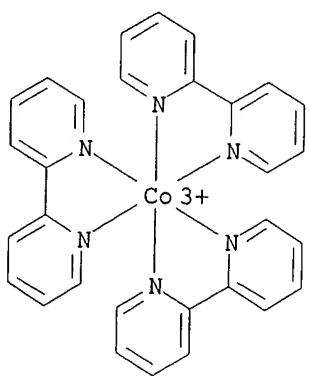
L1 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2003 ACS
RN **174749-62-3** REGISTRY
CN Cobalt(3+), tris(2,2'-bipyridine-N,N')-, (OC-6-11)-, sodium hexafluorophosphate(1-) (OC-6-11)-tris[ethanedioato(2-)-O,O']chromate(3-) (1:1:1:1) (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Chromate(3-), tris[ethanedioato(2-)-O,O']-, (OC-6-11)-, sodium (OC-6-11)-tris(2,2'-bipyridine-N,N')cobalt(3+) hexafluorophosphate(1-) (1:1:1:1) (9CI)
OTHER NAMES:
CN Tris(2,2'-bipyridine)cobalt(3+) tris(oxalato)chromate(3-) sodium hexafluorophosphate(1-)
MF C30 H24 Co N6 . C6 Cr O12 . F6 P . Na
SR CA
LC STN Files: CA, CAPLUS

Ring System Data

| Elemental Analysis | Elemental Sequence | Size of the Rings | Ring System Formula | Ring Identifier | RID Occurrence |
|--------------------|--------------------|-------------------|---------------------|-----------------|----------------|
| EA | ES | SZ | RF | RID | Count |
| C2CrO2- | CroC2O- | 5-5-5 | C6CrO6 | 1523.80.1 | 1 in CM |
| C2CrO2-C2CrO2 | CroC2O-CrO2C2O | | | | 3 |
| C2CoN2- | CoNC2N- | 5-5-5-6-6-6- | C30CoN6 | 13130.7.1 | 1 in CM |
| C2CoN2- | CoNC2N- | 6-6-6 | | | 1 |
| C2CoN2-C5N- | CoNC2N-NC5- | | | | |
| C5N-C5N-C5N- | NC5-NC5-NC5- | | | | |
| C5N-C5N | NC5-NC5 | | | | |

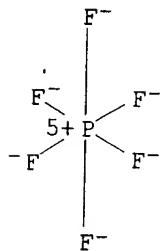
CM 1

CRN 19052-39-2
CMF C30 H24 Co N6
CCI CCS



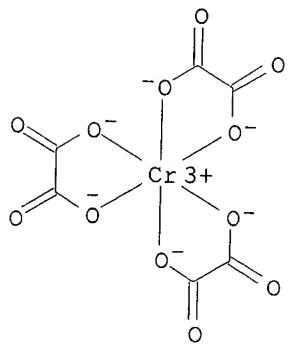
CM 2

CRN 16919-18-9
CMF F6 P
CCI CCS



CM 3

CRN 15054-01-0
CMF C6 Cr O12
CCI CCS



bipyridine oxalatochromate
IT Energy level transition
Energy transfer
Luminescence
Ultraviolet and visible spectra
(of bipyridinechromium oxalatochromate)
IT Crystal structure
Molecular structure
(of chromium/cobalt bipyridine oxalatotransition metalate and chromium phenanthroline dithiooxalatochromate complexes)
IT Imines
RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
(di-, transition metal complexes, oxalatochromate/manganate and dithiooxalatocobaltate; prepn. and crystal structure of)
IT Transition metal compounds
RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
(diimine complexes, oxalatochromate/manganate and dithiooxalatocobaltate; prepn. and crystal structure of)
IT 23539-86-8, Tris(2,2'-bipyridine)chromium(3+) triperchlorate
RL: RCT (Reactant); RACT (Reactant or reagent)
(for prepn. of chromium bipyridine oxalatochromate/manganate complexes)
IT 174749-67-8, Tris(2,2'-bipyridine)chromium(3+)
tris(tetrafluoroborate(1-))
RL: RCT (Reactant); RACT (Reactant or reagent)
(for prepn. of chromium bipyridine oxalatomanganate complexes)
IT 14217-01-7, Tripotassium tris(oxalato)chromate(3-)
RL: RCT (Reactant); RACT (Reactant or reagent)
(for prepn. of chromium/cobalt bipyridine oxalatochromate complexes)
IT 28277-53-4, Tris(2,2'-bipyridine)cobalt(3+) tris(hexafluorophosphate(1-))
RL: RCT (Reactant); RACT (Reactant or reagent)
(for prepn. of cobalt bipyridine oxalatochromate complex)
IT 39016-57-4, Tris(1,10-phenanthroline)nickel(2+) sulfate 92348-93-1
RL: RCT (Reactant); RACT (Reactant or reagent)
(for prepn. of nickel phenanthroline dithiooxalatocobaltate complex)
IT 174749-59-8P, Tris(2,2'-bipyridine)chromium(3+) tris(oxalato)chromate(3-)
sodium perchlorate
RL: PEP (Physical, engineering or chemical process); PRP (Properties);
SPN
(Synthetic preparation); PREP (Preparation); PROC (Process)
(prepn. and crystal structure and photophys. of)
IT 174749-60-1P, Tris(2,2'-bipyridine)chromium(3+)
tris(oxalato)dimanganate(2-)
) perchlorate 174749-62-3P, Tris(2,2'-bipyridine)cobalt(3+)
tris(oxalato)chromate(3-) sodium hexafluorophosphate(1-) 174749-64-5P,
Tris(1,10-phenanthroline)nickel(2+) tris(dithiooxalato)cobaltate(3-)
sodium acetone
RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
(prepn. and crystal structure of)
IT 174749-59-8DP, Tris(2,2'-bipyridine)chromium(3+)
tris(oxalato)chromate(3-)
sodium perchlorate, solid soln. with tris(bipyridine)rhodium analog
174749-66-7DP, Tris(2,2'-bipyridine)rhodium(3+) tris(oxalato)chromate(3-)
sodium perchlorate, solid soln. with tris(bipyridine)chromium analog
RL: PEP (Physical, engineering or chemical process); PRP (Properties);
SPN

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FILE COVERS 1907 - 5 Mar 2003 VOL 138 ISS 10
FILE LAST UPDATED: 4 Mar 2003 (20030304/ED)

This file contains CAS Registry Numbers for easy and accurate substance identification.

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=> s de19933898/pn
L1           1 DE19933898/PN

=> d 11 all

L1  ANSWER 1 OF 1  CAPLUS  COPYRIGHT 2003 ACS
AN  2001:78395  CAPLUS
DN  134:125211
TI  Tris(oxalato)phosphates, method for their preparation and their use
IN  Wietelmann, Ulrich; Schade, Klaus; Lischka, Uwe
PA  Chemetall G.m.b.H., Germany
SO  PCT Int. Appl., 29 pp.
CODEN: PIXXD2
DT  Patent
LA  German
IC  ICM C07F009-6571
ICS H01M010-40
CC  78-7 (Inorganic Chemicals and Reactions)
Section cross-reference(s): 72
FAN.CNT 1
      PATENT NO.      KIND   DATE          APPLICATION NO.    DATE
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PI  WO 2001007450      A1  20010201        WO 2000-EP4301  20000512
      W: CA, CN, JP, KR, US
      RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL,
            PT, SE
      DE 19933898      A1  20010201        DE 1999-19933898 19990722 <--
      EP 1203001       A1  20020508        EP 2000-925279  20000512
      R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,
            IE, FI, CY
      JP 2003505464      T2  20030212        JP 2001-512534  20000512
PRAI DE 1999-19933898      A  19990722
      WO 2000-EP4301      W  20000512
AB  The invention relates to tris(oxalato)phosphates, M[P(C2O4)3] (M = H, metal, N(R1R2R3R4), R1, R2, R3, R4 = independently H, C1-8 alkyl group). The invention also relates to a method for prep. such compds. as well as to their use.
ST  tris oxalato phosphate prep
IT  Quaternary ammonium compounds, preparation
      RL: SPN (Synthetic preparation); PREP (Preparation)
            (prepn. of tris(oxalato)phosphate salts with)
IT  Phosphates, preparation
      RL: SPN (Synthetic preparation); PREP (Preparation)
            (tris(oxalato)phosphates; prepn. of)
IT  321201-34-7P, Hydrogen tris(oxalato)phosphate(1-)
      RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
```

(Reactant or reagent)
(prepn. and reaction with butyllithium)

IT 321201-35-8P, Sodium tris(oxalato)phosphate(1-) 321201-36-9P
321201-37-0P 321201-38-1P 321201-39-2P
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)

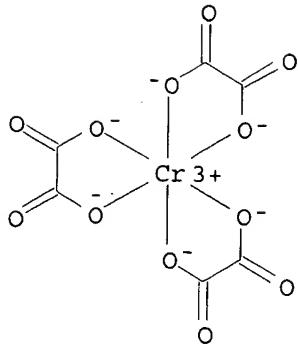
IT 321201-33-6P, Lithium tris(oxalato)phosphate(1-)
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of electrolyte soln. of)

IT 10026-13-8, Phosphorus pentachloride
RL: RCT (Reactant); RACT (Reactant or reagent)
(reaction with oxalic acid)

IT 144-62-7, Oxalic acid, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(reaction with phosphorus pentachloride)

RE.CNT 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD
RE

(1) Handa, M; ELECTROCHEMICAL AND SOLID-STATE LETTERS 1999, V2(2), P60 CAPLUS
(2) Hitachi Maxell Ltd; EP 0631340 A 1994 CAPLUS
(3) Merck Patent Gmbh; WO 9807729 A 1998 CAPLUS



1 REFERENCES IN FILE CA (1962 TO DATE)
 1 REFERENCES IN FILE CAPLUS (1962 TO DATE)

=> filc aplus

FILC IS NOT A RECOGNIZED COMMAND

The previous command name entered was not recognized by the system.
 For a list of commands available to you in the current file, enter
 "HELP COMMANDS" at an arrow prompt (>).

=> fil caplus

| COST IN U.S. DOLLARS | SINCE FILE ENTRY | TOTAL SESSION |
|--|------------------|---------------|
| FULL ESTIMATED COST | 46.30 | 70.31 |
| DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS) | SINCE FILE ENTRY | TOTAL SESSION |
| CA SUBSCRIBER PRICE | 0.00 | -2.60 |

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FILE COVERS 1907 - 27 Jan 2003 VOL 138 ISS 5
 FILE LAST UPDATED: 26 Jan 2003 (20030126/ED)

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> s 17
 L8 3 L7

=> s 18 and tocopherol?
 26227 TOCOPHEROL?
 L9 1 L8 AND TOCOPHEROL?

=> d bib abs

L9 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2003 ACS
AN 2002:573361 CAPLUS
DN 137:125303
TI Manufacture of (all-rac)-.alpha.-tocopherol
IN Bonrath, Werner; Netscher, Thomas; Wietelmann, Ulrich
PA Roche Vitamins A.-G., Switz.
SO Eur. Pat. Appl., 11 pp.
CODEN: EPXXDW
DT Patent
LA English
FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|----------|---|------|----------|-----------------|----------|
| PI | EP 1227089 | A1 | 20020731 | EP 2002-764 | 20020114 |
| | R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR | | | | |
| | JP 2002284776 | A2 | 20021003 | JP 2002-5681 | 20020115 |
| | CN 1365977 | A | 20020828 | CN 2002-102027 | 20020117 |
| | US 2002161247 | A1 | 20021031 | US 2002-53297 | 20020117 |
| PRAI | EP 2001-101026 | A | 20010118 | | |
| OS | CASREACT 137:125303 | | | | |
| AB | A process for the manuf. of (.-+.-).alpha.-tocopherol by the catalyzed reaction of trimethylhydroquinone with isophytol or phytol is characterized by carrying out the reaction in the presence of hydrogen tris(oxalato)phosphate, or an adduct thereof with a solvent, as the catalyst in an org. solvent. The product of the process is the most active and industrially most important member of the vitamin E group. | | | | |
| RE.CNT 3 | THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD ALL CITATIONS AVAILABLE IN THE RE FORMAT | | | | |

=> d bib abs 1-3 18

L8 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2003 ACS
AN 2002:573361 CAPLUS
DN 137:125303
TI Manufacture of (all-rac)-.alpha.-tocopherol
IN Bonrath, Werner; Netscher, Thomas; Wietelmann, Ulrich
PA Roche Vitamins A.-G., Switz.
SO Eur. Pat. Appl., 11 pp.
CODEN: EPXXDW
DT Patent
LA English
FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|----------|---|------|----------|-----------------|----------|
| PI | EP 1227089 | A1 | 20020731 | EP 2002-764 | 20020114 |
| | R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR | | | | |
| | JP 2002284776 | A2 | 20021003 | JP 2002-5681 | 20020115 |
| | CN 1365977 | A | 20020828 | CN 2002-102027 | 20020117 |
| | US 2002161247 | A1 | 20021031 | US 2002-53297 | 20020117 |
| PRAI | EP 2001-101026 | A | 20010118 | | |
| OS | CASREACT 137:125303 | | | | |
| AB | A process for the manuf. of (.-+.-).alpha.-tocopherol by the catalyzed reaction of trimethylhydroquinone with isophytol or phytol is characterized by carrying out the reaction in the presence of hydrogen tris(oxalato)phosphate, or an adduct thereof with a solvent, as the catalyst in an org. solvent. The product of the process is the most active and industrially most important member of the vitamin E group. | | | | |
| RE.CNT 3 | THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD | | | | |

ALL CITATIONS AVAILABLE IN THE RE FORMAT

L8 ANSWER 2 OF 3 CAPLUS COPYRIGHT 2003 ACS
 AN 2001:78395 CAPLUS
 DN 134:125211
 TI Tris(oxalato)phosphates, method for their preparation and their use
 IN Wietelmann, Ulrich; Schade, Klaus; Lischka, Uwe
 PA Chemetall G.m.b.H., Germany
 SO PCT Int. Appl., 29 pp.
 CODEN: PIXXD2
 DT Patent
 LA German
 FAN.CNT 1

*2001 Date - Sel equivalents
for potential to 2(e)*

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|--|--|----------|------------------|----------|
| PI WO 2001007450 | A1 | 20010201 | WO 2000-EP4301 | 20000512 |
| W: CA, CN, JP, KR, US | | | | |
| RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE | | | | |
| → DE 19933898 | A1 | 20010201 | DE 1999-19933898 | 19990722 |
| → EP 1203001 | A1 | 20020508 | EP 2000-925279 | 20000512 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, FI, CY | | | | |
| PRAI DE 1999-19933898 | A | 19990722 | | |
| WO 2000-EP4301 | W | 20000512 | | |
| AB The invention relates to tris(oxalato)phosphates, M[P(C ₂ O ₄) ₃] (M = H, metal, N(R ₁ R ₂ R ₃ R ₄), R ₁ , R ₂ , R ₃ , R ₄ = independently H, C ₁₋₈ alkyl group). The invention also relates to a method for prep. such compds. as well as to their use. | | | | |
| RE.CNT 3 | THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD | | | |
| | ALL CITATIONS AVAILABLE IN THE RE FORMAT | | | |

L8 ANSWER 3 OF 3 CAPLUS COPYRIGHT 2003 ACS
 AN 1996:121444 CAPLUS
 DN 124:248655
 TI Chiral, Three-Dimensional Supramolecular Compounds: Homo- and Bimetallic Oxalate- and 1,2-Dithiooxalate-Bridged Networks. A Structural and Photophysical Study
 AU Decurtins, Silvio; Schmalle, Helmut W.; Pellaux, Rene; Schneuwly, Philippe; Hauser, Andreas
 CS Institut fuer Anorganische Chemie, Universitaet Zuerich, Zurich, CH-8057, Switz.
 SO Inorganic Chemistry (1996), 35(6), 1451-60
 CODEN: INOCAJ; ISSN: 0020-1669
 PB American Chemical Society
 DT Journal
 LA English
 AB In analogy to the [MII(bpy)₃]²⁺ cations (MII = transition-metal; bpy = 2,2'-bipyridine), [MIII(bpy)₃]³⁺ cations (MIII = Cr or Co) induce the crystn. of chiral, anionic three-dimensional (3D) coordination polymers of oxalate-bridged (.mu.-ox) metal complexes [MII₂(ox)₃]_n2n⁻ or [MIMIII(ox)₃]_n2n⁻. The tripos. charge is partially compensated by inclusion of addnl. complex anions like ClO₄⁻, BF₄⁻, or PF₆⁻ which are encapsulated in cubic shaped cavities formed by the bipyridine ligands of the cations. Thus, an elaborate structure of cationic and anionic species within a polymeric anionic network is realized. The compds. isolated and structurally characterized include [Cr(bpy)₃][ClO₄]⁻ [NaCr(ox)₃]⁻ (1), [Cr(bpy)₃][ClO₄]⁻ [Mn₂(ox)₃]⁻ (2), [Cr(bpy)₃][BF₄]⁻ [Mn₂(ox)₃]⁻ (3), [Co(bpy)₃][PF₆]⁻ [NaCr(ox)₃]⁻ (4). Crystal data: 1, cubic, space group P213, a 15.523(4) .ANG., Z = 4; 2, cubic, space group P4132, a 15.564(3) .ANG., Z = 4; 3, cubic, P4132, a 15.553(3) .ANG., Z = 4; 4, cubic, P213, a 15.515(3) .ANG., Z = 4. Also, it seemed likely that 1,2-dithiooxalate (dto) could act as an alternative to the oxalate bridging ligand, and as a

result [Ni(phen)3][NaCo(dto)3].cntdot.C3H6O (5) has successfully been isolated and structurally characterized. Crystal data: 5, orthorhombic, space group P212121, a 16.238(4), b 16.225(4), c 18.371(5) .ANG., Z = 4. The photophys. properties of 1 were studied. In single crystal absorption spectra of [Cr(bpy)3][ClO₄] [NaCr(ox)3] (1), the spin-flip transitions of both the [Cr(bpy)3]³⁺ and the [Cr(ox)₃]³⁻ chromophores are obsd. and can be clearly distinguished. Irradiating into the spin-allowed 4A₂ .fwdarw. 4T₂ absorption band of [Cr(ox)₃]³⁻ results in intense luminescence from the 2E state of [Cr(bpy)3]³⁺ as a result of rapid energy transfer processes.

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<http://www.cas.org/ONLINE/STN/STNOTES/stnotes27.pdf>

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FILE COVERS 1907 - 21 Jan 2003 VOL 138 ISS 4
FILE LAST UPDATED: 20 Jan 2003 (20030120/ED)

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> d que 119
L12 22 SEA FILE=REGISTRY ABB=ON (10026-13-8/BI OR 10191-41-0/BI OR 105-58-8/BI OR 108-10-1/BI OR 108-32-7/BI OR 108-88-3/BI OR 110-54-3/BI OR 111-65-9/BI OR 120-92-3/BI OR 1330-20-7/BI OR 142-82-5/BI OR 144-62-7/BI OR 321201-34-7/BI OR 60046-87-9/BI OR 616-38-6/BI OR 700-13-0/BI OR 71-43-2/BI OR 7541-49-3/BI OR 78-59-1/BI OR 96-22-0/BI OR 96-48-0/BI OR 96-49-1/BI)
L13 1 SEA FILE=REGISTRY ABB=ON 10191-41-0 - *α tocopherol*
L14 1032 SEA FILE=HCAPLUS ABB=ON L13
L15 104 SEA FILE=HCAPLUS ABB=ON L14(L)(PREP OR IMF OR SPN)/RL
L16 2 SEA FILE=REGISTRY ABB=ON L12 AND 1/P
L17 1 SEA FILE=REGISTRY ABB=ON L16 AND PHOSPHATE? *Catalyst*

L18 2 SEA FILE=HCAPLUS ABB=ON L17
 L19 1 SEA FILE=HCAPLUS ABB=ON L15 AND L18

=> d 119 all hitstr

L19 ANSWER 1 OF 1 HCAPLUS COPYRIGHT 2003 ACS
 AN 2002:573361 HCAPLUS
 DN 137:125303
 TI Manufacture of (all-rac)-.alpha.-tocopherol
 IN Bonrath, Werner; Netscher, Thomas; Wietelmann, Ulrich
 PA Roche Vitamins A.-G., Switz.
 SO Eur. Pat. Appl., 11 pp.
 CODEN: EPXXDW
 DT Patent
 LA English
 IC ICM C07D311-72
 CC 30-20 (Terpenes and Terpenoids)
 Section cross-reference(s): 29, 67

FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|--|------|----------|-----------------|----------|
| PI | EP 1227089 | A1 | 20020731 | EP 2002-764 | 20020114 |
| | R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR | | | | |
| | JP 2002284776 | A2 | 20021003 | JP 2002-5681 | 20020115 |
| | CN 1365977 | A | 20020828 | CN 2002-102027 | 20020117 |
| | US 2002161247 | A1 | 20021031 | US 2002-53297 | 20020117 |
| PRAI | EP 2001-101026 | A | 20010118 | | |
| OS | CASREACT 137:125303 | | | | |

AB A process for the manuf. of (.-+.-).alpha.-tocopherol by the catalyzed reaction of trimethylhydroquinone with isophytol or phytol is characterized by carrying out the reaction in the presence of hydrogen tris(oxalato)phosphate, or an adduct thereof with a solvent, as the catalyst in an org. solvent. The product of the process is the most active and industrially most important member of the vitamin E group.

ST tocopherol prepn hydrogen trisoxalatophosphate catalyst

IT 321201-34-7P, Hydrogen tris(oxalato)phosphate(1-)

RL: CAT (Catalyst use); IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)
 (process for the prepn. of .alpha.-tocopherol)

IT 10191-41-0P, (.-+.-).alpha.-Tocopherol

RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
 (process for the prepn. of .alpha.-tocopherol)

IT 71-43-2, Benzene, uses 78-59-1, Isophorone 96-22-0, Diethyl ketone 96-48-0, .gamma.-Butyrolactone 96-49-1, Ethylene carbonate 105-58-8, Diethyl carbonate 108-10-1, Isobutyl methyl ketone 108-32-7, Propylene carbonate 108-88-3, Toluene, uses 110-54-3, Hexane, uses 111-65-9, Octane, uses 120-92-3, Cyclopentanone 142-82-5, Heptane, uses 616-38-6, Dimethyl carbonate 1330-20-7, Xylene, uses RL: NUU (Other use, unclassified); USES (Uses)

(process for the prepn. of .alpha.-tocopherol)

IT 144-62-7, Oxalic acid, reactions 700-13-0, Trimethylhydroquinone 7541-49-3 10026-13-8, Phosphorus pentachloride 60046-87-9

RL: RCT (Reactant); RACT (Reactant or reagent)

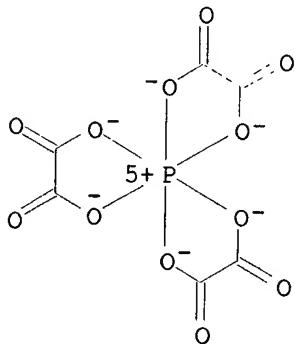
(process for the prepn. of .alpha.-tocopherol)

RE.CNT 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD
 RE

(1) Hoffmann La Roche; EP 0784042 A 1997 HCAPLUS

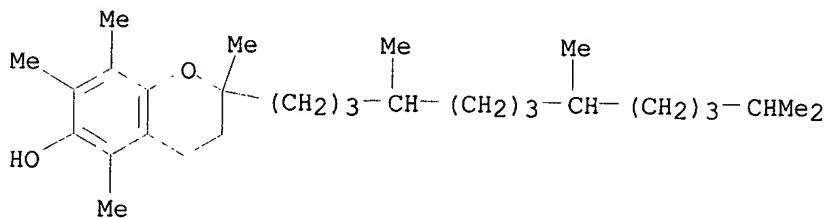
applicante

(2) Lamande, L; JOURNAL OF ORGANOMETALLIC CHEMISTRY 1987, V329(1), P1 HCAPLUS
 (3) Von Werder, F; US 2230659 A 1941 HCAPLUS
 IT 321201-34-7P, Hydrogen tris(oxalato)phosphate(1-)
 RL: CAT (Catalyst use); IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)
 (process for the prepn. of .alpha.-tocopherol)
 RN 321201-34-7 HCAPLUS
 CN Phosphate(1-), tris[ethanedioato(2-)-.kappa.O1,.kappa.O2]-, hydrogen,
 (OC-6-11)- (9CI) (CA INDEX NAME)



● H⁺

IT 10191-41-0P, (.+-.)-.alpha.-Tocopherol
 RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
 (process for the prepn. of .alpha.-tocopherol)
 RN 10191-41-0 HCAPLUS
 CN 2H-1-Benzopyran-6-ol, 3,4-dihydro-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)- (9CI) (CA INDEX NAME)



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L12 22 SEA FILE=REGISTRY ABB=ON (10026-13-8/BI OR 10191-41-0/BI OR 105-58-8/BI OR 108-10-1/BI OR 108-32-7/BI OR 108-88-3/BI OR 110-54-3/BI OR 111-65-9/BI OR 120-92-3/BI OR 1330-20-7/BI OR 142-82-5/BI OR 144-62-7/BI OR 321201-34-7/BI OR 60046-87-9/BI OR 616-38-6/BI OR 700-13-0/BI OR 71-43-2/BI OR 7541-49-3/BI OR 78-59-1/BI OR 96-22-0/BI OR 96-48-0/BI OR 96-49-1/BI)
 L13 1 SEA FILE=REGISTRY ABB=ON 10191-41-0
 L14 1032 SEA FILE=HCAPLUS ABB=ON L13

*Remaining prep's of
 & tocopherol
 starting
 with
 hydroquinone
 +
 phytol
 and any
 catalyst*

L15 104 SEA FILE=HCAPLUS ABB=ON L14(L) (PREP OR IMF OR SPN)/RL
 L16 2 SEA FILE=REGISTRY ABB=ON L12 AND 1/P
 L17 1 SEA FILE=REGISTRY ABB=ON L16 AND PHOSPHATE?
 L18 2 SEA FILE=HCAPLUS ABB=ON L17
 L19 1 SEA FILE=HCAPLUS ABB=ON L15 AND L18
 L20 59 SEA FILE=HCAPLUS ABB=ON L15 AND ?PHYTOL?
 L21 1 SEA FILE=REGISTRY ABB=ON L12 AND HYDROQUINONE
 L22 687 SEA FILE=HCAPLUS ABB=ON L21
 L23 48 SEA FILE=HCAPLUS ABB=ON L20 AND L22
 L24 24 SEA FILE=HCAPLUS ABB=ON L23 AND CAT/RL
 L25 23 SEA FILE=HCAPLUS ABB=ON L24 NOT L19

=> d 125 1-23 all

L25 ANSWER 1 OF 23 HCAPLUS COPYRIGHT 2003 ACS
 AN 2002:332181 HCAPLUS
 DN 136:340853
 TI Method for preparing dl-alpha-tocopherol with high yield
 IN Kim, Jeong-Soo; Cheong, Heui-Young; Lee, Sijoon
 PA SK Corporation, S. Korea
 SO PCT Int. Appl., 17 pp.
 CODEN: PIXXD2
 DT Patent
 LA English
 IC ICM C07D311-74
 CC 30-20 (Terpenes and Terpenoids)
 Section cross-reference(s): 67
 FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|--|------|----------|-----------------|----------|
| PI | WO 2002034738 | A1 | 20020502 | WO 2000-KR1201 | 20001023 |
| | W: CN, JP | | | | |
| | RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE | | | | |
| PRAI | US 6384245 | B1 | 20020507 | US 2000-697615 | 20001026 |
| OS | WO 2000-KR1201 | A | 20001023 | | |
| AB | The invention discloses a method for prep. DL-.alpha.-tocopherol (I) with a high yield through the condensation of isophytol or phytol derivs. with trimethylhydroquinone (TMHQ) in the presence of a Zn-Al heterogeneous catalyst system. At 80 to 120 .degree.C, the condensation is carried out for 2 to 7 h in the presence of a Zn(II) ion-coated alumina-silica catalyst in an n-heptane solvent. The synthetic Zn(II) ion-coated silica-alumina synthetic catalyst system can remarkably reduce side-reactions upon the condensation of isophytol or phytol derivs. and TMHQ, thus producing I with a high purity at a high yield. In addn., the catalyst system is greatly convenient to handle and therefore apply for continuous reactions for the prepn. of I. With these advantages, the catalyst system can be effectively used in prep. highly pure I at a high yield on a com. scale. | | | | |
| ST | tocopherol prepn zinc aluminum heterogeneous catalyst; isophytol phytol deriv trimethylhydroquinone condensation tocopherol prepn | | | | |
| IT | Tocopherols | | | | |
| | RL: SPN (Synthetic preparation); PREP (Preparation) (method for prep. tocopherol via condensation of isophytol or phytol derivs. with trimethylhydroquinone in the presence of a Zn-Al heterogeneous catalyst system) | | | | |
| IT | Catalysts Condensation reaction catalysts | | | | |

(zinc-aluminum; in prepg. tocopherol via condensation of **isophytol** or **phytol** derivs. with trimethylhydroquinone in the presence of a Zn-Al heterogeneous catalyst system)

IT 10191-41-0P, DL-.alpha.-Tocopherol

RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)

(method for prepg. tocopherol via condensation of **isophytol** or **phytol** derivs. with trimethylhydroquinone in the presence of a Zn-Al heterogeneous catalyst system)

IT 150-86-7, Phytol 505-32-8, Isophytol

700-13-0, Trimethylhydroquinone 58425-36-8

RL: RCT (Reactant); RACT (Reactant or reagent)

(method for prepg. tocopherol via condensation of **isophytol** or **phytol** derivs. with trimethylhydroquinone in the presence of a Zn-Al heterogeneous catalyst system)

IT 7646-85-7, Zinc chloride, uses

RL: CAT (Catalyst use); USES (Uses)

(silica-alumina bound; method for prepg. tocopherol via condensation of **isophytol** or **phytol** derivs. with trimethylhydroquinone in the presence of a Zn-Al heterogeneous catalyst system)

IT 159995-97-8, Aluminum silicon oxide

RL: CAT (Catalyst use); USES (Uses)

(zinc chloride coated; method for prepg. tocopherol via condensation of **isophytol** or **phytol** derivs. with trimethylhydroquinone in the presence of a Zn-Al heterogeneous catalyst system)

IT 10236-16-5, Phytol acetate

RL: RCT (Reactant); RACT (Reactant or reagent)

(zinc chloride coated; method for prepg. tocopherol via condensation of **isophytol** or **phytol** derivs. with trimethylhydroquinone in the presence of a Zn-Al heterogeneous catalyst system)

RE.CNT 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD

RE

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- (2) Kuraray Co; US 4252726 A 1981 HCPLUS
- (3) Mitsui Toatsu Chem Inc; JP 59190987 A 1984 HCPLUS
- (4) Nissin Flour Milling Co; US 4217285 A 1980 HCPLUS
- (5) Sk Corporation; KR 019754 A 2001

L25 ANSWER 2 OF 23 HCPLUS COPYRIGHT 2003 ACS

AN 2002:239437 HCPLUS

DN 137:109397

TI Synthesis of (all-rac)-.alpha.-tocopherol using fluorinated NH-acidic catalysts

AU Bonrath, Werner; Haas, Alois; Hoppmann, Eike; Netscher, Thomas; Pauling, Horst; Schager, Frank; Wildermaann, Angela

CS Research and Development, Roche Vitamins Ltd, Basel, 4070, Switz.

SO Advanced Synthesis & Catalysis (2002), 344(1), 37-39
CODEN: ASCAF7; ISSN: 1615-4150

PB Wiley-VCH Verlag GmbH

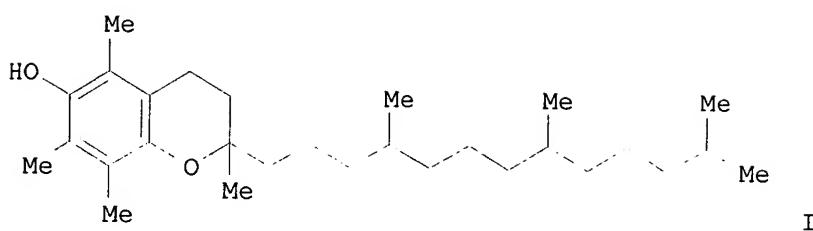
DT Journal

LA English

CC 30-30 (Terpenes and Terpenoids)

OS CASREACT 137:109397

GI



- AB The synthesis of (all-rac)-.alpha.-tocopherol (I) starting from trimethylhydroquinone and **isophytol** using fluorinated NH-acidic catalysts is described. The scope and limitations of this type of catalyst are discussed. The advantages of this new procedure are high yield and selectivity, no waste problem and mild reaction conditions. The best results in the synthesis of I (94% yield) using NH-acidic compds. are obtained in polar solvents. The used catalyst could be recovered.
- ST tocopherol prepn trimethylhydroquinone **isophytol** Friedel Crafts alkylation biphasic catalyst; ring closure catalyst biphasic tocopherol prepn trimethylhydroquinone **isophytol**; fluorinated NH acid catalyst tocopherol prepn
- IT Cyclization catalysts
Friedel-Crafts reaction catalysts
(synthesis of (all-rac)-.alpha.-tocopherol using fluorinated NH-acidic catalysts)
- IT Cyclization
Friedel-Crafts reaction
(synthesis of (all-rac)-.alpha.-tocopherol using fluorinated NH-acidic catalysts via)
- IT 1535-93-9 39847-37-5 39847-38-6 39847-39-7 39847-40-0 39847-41-1
82113-65-3 84246-29-7 152894-10-5 152894-12-7 200728-68-3
400608-35-7 400608-36-8
RL: **CAT (Catalyst use); USES (Uses)**
(synthesis of (all-rac)-.alpha.-tocopherol using fluorinated NH-acidic catalysts)
- IT 96-22-0, Diethyl ketone 96-48-0, .gamma.-Butyrolactone 96-49-1,
Ethylene carbonate 108-32-7, Propylene carbonate 108-88-3, Toluene,
uses 142-82-5, Heptane, uses
RL: NUU (Other use, unclassified); USES (Uses)
(synthesis of (all-rac)-.alpha.-tocopherol using fluorinated NH-acidic catalysts)
- IT 700-13-0 60046-87-9 - *hydroquinone*
RL: RCT (Reactant); RACT (Reactant or reagent)
(synthesis of (all-rac)-.alpha.-tocopherol using fluorinated NH-acidic catalysts)
- IT 10191-41-0P *alpha tocopherol*
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(synthesis of (all-rac)-.alpha.-tocopherol using fluorinated NH-acidic catalysts)
- IT 52225-20-4P
RL: SPN (Synthetic preparation); PREP (Preparation)
(synthesis of (all-rac)-.alpha.-tocopherol using fluorinated NH-acidic catalysts)
- RE.CNT 25 THERE ARE 25 CITED REFERENCES AVAILABLE FOR THIS RECORD
RE
(1) Anon; Chemical Market Reporter 1997, P5

- (2) Aquino, F; Appl Catal A: General 2001, V220, P51
- (3) Baak, M; WO 9821197 1998 HCPLUS
- (4) Baldenius, K; Ullmann's Encyclopedia of Industrial Chemistry 1996, VA27, P478
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- (16) Matsui, M; Bull Chem Soc Jpn 1995, V68, P3569 HCPLUS
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- (24) Schulz, B; DE 3203487 A1 1983 HCPLUS
- (25) Wang, S; J Supercrit Fluids 2000, V17, P135 HCPLUS

L25 ANSWER 3 OF 23 HCPLUS COPYRIGHT 2003 ACS
AN 2002:138923 HCPLUS
DN 136:183967
TI Process for manufacturing all-rac.-.alpha.-tocopherol in the presence of a bis(perfluoroalkanesulfonyl or pentafluorobenzenesulfonyl)imide catalyst
IN Bonrath, Werner; Haas, Alois; Hoppmann, Eike; Pauling, Horst
PA Roche Vitamins A.-G., Switz.
SO Eur. Pat. Appl., 10 pp.
CODEN: EPXXDW
DT Patent
LA English
IC ICM C07D311-72
CC 30-20 (Terpenes and Terpenoids)
Section cross-reference(s): 67
FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|--|------|----------|-----------------|----------|
| PI | EP 1180517 | A1 | 20020220 | EP 2001-119322 | 20010810 |
| | R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO | | | | |
| | BR 2001003412 | A | 20020326 | BR 2001-3412 | 20010816 |
| | JP 2002128775 | A2 | 20020509 | JP 2001-246843 | 20010816 |
| | US 2002072619 | A1 | 20020613 | US 2001-931663 | 20010816 |
| | US 6482961 | B2 | 20021119 | | |
| | CN 1339437 | A | 20020313 | CN 2001-125595 | 20010817 |
| PRAI | EP 2000-117761 | A | 20000818 | | |
| OS | CASREACT 136:183967; MARPAT 136:183967 | | | | |
| AB | A process, for the manuf. of all-racemic-.alpha.-tocopherol (I) via the acid-catalyzed condensation of trimethylhydroquinone with phytol or isophytol , is characterized by carrying out the condensation in the presence of a bis(perfluorohydrocarbyl)imide or a metal bis(perfluorohydrocarbyl)imide, [(R ₁ SO ₂) ₃ N] _x R ₂ [R ₁ = perfluoroalkyl, C _n F _{2n+1} , pentafluorophenyl; R ₂ = H, B, Mg, Al, Si, Sc, Ti, V, VO, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Rh, Pd, Ag, Sn, La, Ce, Pr, Nd, Eu, Dy, Yb, Hf, Pt, | | | | |

Au; n = 1 - 10; x = valency of proton (1) or metal cation (1-4)], as a catalyst in an org. solvent. Thus, trimethylhydroquinone was suspended in PhMe and catalytic bis(pentafluoroethanesulfonyl)amine was added, after heating to 50-150.degree., **isophytol** was added over 20 mins., after 30 mins. more, the solvent is removed, giving 89.6% crude I.

ST tocopherol alpha manufg process; trisperfluoroalkanesulfonyl catalyst manufg process alpha tocopherol; trimethylhydroquinone condensation **isophytol phytol** bisulfonylimide catalyst; imide bisperfluoroalkanesulfonyl catalyst manufg process alpha tocopherol

IT Hydrocarbons, uses

RL: NUU (Other use, unclassified); USES (Uses)
(aliph. or arom., solvent; process for manufg. all-rac.-.alpha.-tocopherol by acid-catalyzed condensation of trimethylhydroquinone with **phytol** or **isophytol** in the presence of a bis(perfluoroalkanesulfonyl)imide catalyst)

IT Ketones, uses

RL: NUU (Other use, unclassified); USES (Uses)
(aliph. or cyclic, solvent; process for manufg. all-rac.-.alpha.-tocopherol by acid-catalyzed condensation of trimethylhydroquinone with **phytol** or **isophytol** in the presence of a bis(perfluoroalkanesulfonyl)imide catalyst)

IT Bronsted acids

RL: CAT (Catalyst use); USES (Uses)
(co-catalyst; process for manufg. all-rac.-.alpha.-tocopherol by acid-catalyzed condensation of trimethylhydroquinone with **phytol** or **isophytol** in the presence of a bis(perfluoroalkanesulfonyl)imide catalyst)

IT Carboxylic acids, uses

RL: NUU (Other use, unclassified); USES (Uses)
(esters, aliph. or cyclic, solvent; process for manufg. all-rac.-.alpha.-tocopherol by acid-catalyzed condensation of trimethylhydroquinone with **phytol** or **isophytol** in the presence of a bis(perfluoroalkanesulfonyl)imide catalyst)

IT Condensation reaction

Condensation reaction catalysts

(process for manufg. all-rac.-.alpha.-tocopherol by acid-catalyzed condensation of trimethylhydroquinone with **phytol** or **isophytol** in the presence of a bis(perfluoroalkanesulfonyl)imide catalyst)

IT Metals, uses

RL: CAT (Catalyst use); USES (Uses)
(trisulfonylimide catalysts; process for manufg. all-rac.-.alpha.-tocopherol by acid-catalyzed condensation of trimethylhydroquinone with **phytol** or **isophytol** in the presence of a bis(perfluoroalkanesulfonyl)imide catalyst)

IT 1535-93-9 39847-37-5 39847-38-6 39847-39-7 39847-40-0 39847-41-1
84246-29-7 84331-53-3 152894-10-5 152894-12-7 192888-07-6
200728-68-3 213342-85-9 296280-11-0 400608-35-7 400608-36-8
400608-37-9 400629-85-8 400629-88-1 400629-90-5 400630-94-6
400630-96-8

RL: CAT (Catalyst use); USES (Uses)
(process for manufg. all-rac.-.alpha.-tocopherol by acid-catalyzed condensation of trimethylhydroquinone with **phytol** or **isophytol** in the presence of a bis(perfluoroalkanesulfonyl)imide catalyst)

IT 10191-41-0P

RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
(process for manufg. all-rac.-.alpha.-tocopherol by acid-catalyzed condensation of trimethylhydroquinone with **phytol** or

isophytol in the presence of a bis(perfluoroalkanesulfonyl or pentafluorobenzenesulfonyl)imide catalyst)

IT 150-86-7, **Phytol** 505-32-8, **Isophytol**

700-13-0, Trimethylhydroquinone

RL: RCT (Reactant); RACT (Reactant or reagent)

(process for manufg. all-rac.-.alpha.-tocopherol by acid-catalyzed condensation of trimethylhydroquinone with **phytol** or **isophytol** in the presence of a bis(perfluoroalkanesulfonyl or pentafluorobenzenesulfonyl)imide catalyst)

IT 71-43-2, Benzene, uses 78-59-1, Isophorone 96-22-0, Diethyl ketone 96-48-0, .gamma.-Butyrolactone 96-49-1, Ethylene carbonate 108-10-1, Isobutyl methyl ketone 108-21-4, Isopropyl acetate 108-32-7, Propylene carbonate 108-88-3, Toluene, uses 110-54-3, Hexane, uses 111-65-9, Octane, uses 120-92-3, Cyclopentanone 141-78-6, Ethyl acetate, uses 142-82-5, Heptane, uses 1330-20-7, Xylene, uses

RL: NUU (Other use, unclassified); USES (Uses)

(solvent; process for manufg. all-rac.-.alpha.-tocopherol by acid-catalyzed condensation of trimethylhydroquinone with **phytol** or **isophytol** in the presence of a bis(perfluoroalkanesulfonyl or pentafluorobenzenesulfonyl)imide catalyst)

RE.CNT 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD

RE

- (1) Hoffman La Roche; WO 9821197 A 1998 HCPLUS
- (2) Hoffman La Roche; EP 1000940 A 2000 HCPLUS
- (3) Kazuaki, I; SYNLETT 1996, P1045

L25 ANSWER 4 OF 23 HCPLUS COPYRIGHT 2003 ACS

AN 2001:691767 HCPLUS

DN 135:257368

TI Process for manufacturing all-rac.-.alpha.-tocopherol in the presence of a tris(perfluoroalkanesulfonyl or pentafluorobenzenesulfonyl)methane catalyst

IN Bonrath, Werner; Haas, Alois; Hoppmann, Eike; Netscher, Thomas; Pauling, Horst

PA F. Hoffmann-La Roche A.-G., Switz.

SO Eur. Pat. Appl., 9 pp.

CODEN: EPXXDW

DT Patent

LA English

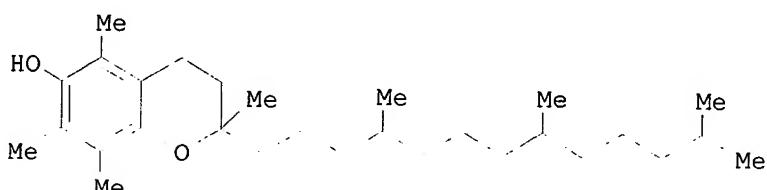
IC ICM C07D311-72

CC 30-20 (Terpenes and Terpenoids)

Section cross-reference(s): 29, 67

FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|---|------|----------|-----------------|----------|
| PI | EP 1134218 | A1 | 20010919 | EP 2001-105979 | 20010310 |
| | R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO | | | | |
| | US 2001027255 | A1 | 20011004 | US 2001-802272 | 20010308 |
| | US 6369242 | B2 | 20020409 | | |
| | CA 2340518 | AA | 20010917 | CA 2001-2340518 | 20010313 |
| | JP 2001294584 | A2 | 20011023 | JP 2001-71442 | 20010314 |
| | BR 2001001075 | A | 20011106 | BR 2001-1075 | 20010315 |
| | CN 1314354 | A | 20010926 | CN 2001-111398 | 20010316 |
| PRAI | EP 2000-105672 | A | 20000317 | | |
| OS | CASREACT 135:257368; MARPAT 135:257368 | | | | |
| GI | | | | | |



- AB A process, for the manuf. of all-racemic-.alpha.-tocopherol (I) via the acid-catalyzed condensation of trimethylhydroquinone with **phytol** or **isophytol**, is characterized by carrying out the condensation in the presence of a tris(perfluoroalkanesulfonyl or pentafluorobenzenesulfonyl)methane or a metal tris(perfluoroalkanesulfonyl or pentafluorobenzenesulfonyl)methide, [(R₁SO₂)₃C]_xR₂ [R₁ = perfluoroalkyl, C_nF_{2n+1}, pentafluorophenyl; R₂ = H, B, Mg, Al, Si, Sc, Ti, V, VO, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Rh, Pd, Ag, Sn, La, Ce, Pr, Nd, Eu, Dy, Yb, Hf, Pt, Au; n = 1 - 10; x = valency of proton (1) or metal cation (1 - 4)], as a catalyst in an org. solvent. Thus, trimethylhydroquinone was suspended in PhMe and catalytic tris(trifluoromethanesulfonyl)methane was added, after heating to 100.degree., **isophytol** was added over 60 mins., after 30 mins. more, the solvent is removed, giving 91.7% crude I.
- ST tocopherol alpha manufg process; trispentafluorobenzenesulfonylmethane catalyst manufg process alpha tocopherol; trisperfluoroalkanesulfonylmethane catalyst manufg process alpha tocopherol; trimethylhydroquinone condensation **isophytol** **phytol** trisulfonylmethane catalyst; tristrifluoromethanesulfonylmethane catalyst manufg process alpha tocopherol; methide trisperfluoroalkanesulfonyl catalyst manufg process alpha tocopherol
- IT Hydrocarbons, uses
RL: NUU (Other use, unclassified); USES (Uses)
(aliph. or arom., solvent; prepn. of all-rac.-alpha-tocopherol via condensation of trimethylhydroquinone with **isophytol** in the presence of a trisulfonylmethane catalyst)
- IT Ketones, uses
RL: NUU (Other use, unclassified); USES (Uses)
(aliph. or cyclic, solvent; prepn. of all-rac.-alpha-tocopherol via condensation of trimethylhydroquinone with **isophytol** in the presence of a trisulfonylmethane catalyst)
- IT Bronsted acids
RL: CAT (Catalyst use); USES (Uses)
(co-catalyst; prepn. of all-rac.-alpha-tocopherol via condensation of trimethylhydroquinone with **isophytol** in the presence of a trisulfonylmethane catalyst)
- IT Carboxylic acids, uses
RL: NUU (Other use, unclassified); USES (Uses)
(esters, aliph. or cyclic, solvent; prepn. of all-rac.-alpha-tocopherol via condensation of trimethylhydroquinone with **isophytol** in the presence of a trisulfonylmethane catalyst)
- IT Solvents
(org.; prepn. of all-rac.-alpha-tocopherol via condensation of trimethylhydroquinone with **isophytol** in the presence of a trisulfonylmethane catalyst)
- IT Condensation reaction
Condensation reaction catalysts
(prepn. of all-rac.-alpha-tocopherol via condensation of trimethylhydroquinone with **isophytol** in the presence of a

trisulfonylmethane catalyst)

IT Metals, uses
 RL: CAT (Catalyst use); USES (Uses)
 (trisulfonylmethide catalysts; prepn. of all-rac.-alpha-tocopherol via condensation of trimethylhydroquinone with **isophytol** in the presence of a trisulfonylmethane catalyst)

IT 7664-38-2, Phosphoric acid, uses 7664-93-9, Sulfuric acid, uses
 RL: CAT (Catalyst use); USES (Uses)
 (co-catalyst; prepn. of all-rac.-alpha-tocopherol via condensation of trimethylhydroquinone with **isophytol** in the presence of a trisulfonylmethane catalyst)

IT 104-15-4, p-Toluenesulfonic acid, uses 60805-12-1,
 Tris(trifluoromethanesulfonyl)methane 114395-71-0 261728-13-6
 360574-09-0 360574-11-4 360574-12-5D, metal salts 361343-17-1
 361343-18-2
 RL: CAT (Catalyst use); USES (Uses)
 (prepn. of all-rac.-alpha-tocopherol via condensation of trimethylhydroquinone with **isophytol** in the presence of a trisulfonylmethane catalyst)

IT 10191-41-0P, (.+-.)-alpha.-Tocopherol
 RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. of all-rac.-alpha-tocopherol via condensation of trimethylhydroquinone with **isophytol** in the presence of a trisulfonylmethane catalyst)

IT 150-86-7, **Phytol** 505-32-8, **Isophytol**
 700-13-0, 2,3,5-Trimethyl-1,4-hydroquinone
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (prepn. of all-rac.-alpha-tocopherol via condensation of trimethylhydroquinone with **isophytol** in the presence of a trisulfonylmethane catalyst)

IT 71-43-2, Benzene, uses 78-59-1, Isophorone 96-22-0, Diethyl ketone 96-48-0, .gamma.-Butyrolactone 96-49-1, Ethylene carbonate 108-10-1, Isobutyl methyl ketone 108-21-4, Isopropyl acetate 108-32-7, Propylene carbonate 108-88-3, Toluene, uses 110-54-3, Hexane, uses 111-65-9, Octane, uses 120-92-3, Cyclopentanone 141-78-6, Ethyl acetate, uses 142-82-5, Heptane, uses 1330-20-7, Xylene, uses
 RL: NUU (Other use, unclassified); USES (Uses)
 (solvent; prepn. of all-rac.-alpha-tocopherol via condensation of trimethylhydroquinone with **isophytol** in the presence of a trisulfonylmethane catalyst)

RE.CNT 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD
 RE

- (1) Eisai Co; EP 0658552 A 1995 HCPLUS
- (2) Hoffmann-La Roche, F; WO 9821197 A 1998 HCPLUS
- (3) Hoffmann-La Roche, F; EP 0949255 A 1999 HCPLUS
- (4) Hoffmann-La Roche, F; EP 1000940 A 2000 HCPLUS
- (5) Minnesota Mining And Manufacturing Company; US 5554664 A 1996 HCPLUS

L25 ANSWER 5 OF 23 HCPLUS COPYRIGHT 2003 ACS
 AN 2001:453047 HCPLUS
 DN 135:61459
 TI Method for preparing dl-alpha-tocopherol with a high yield and high purity
 IN Lee, Sijoon; Kim, Jeong-soo; Yoon, Young-seek; Kim, Myung-jun; Choi, Jun-tae; Kwak, Byong-sung
 PA SK Corp., S. Korea
 SO PCT Int. Appl., 28 pp.
 CODEN: PIXXD2
 DT Patent
 LA English

IC ICM C07D311-74
 CC 30-20 (Terpenes and Terpenoids)
 Section cross-reference(s): 67
 FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|---|------|----------|-----------------|----------|
| PI | WO 2001044224 | A1 | 20010621 | WO 2000-KR1314 | 20001116 |
| | W: CN, JP | | | | |
| | RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR | | | | |
| | US 6441200 | B1 | 20020827 | US 2000-711824 | 20001113 |
| | EP 1237885 | A1 | 20020911 | EP 2000-981848 | 20001116 |
| | R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR | | | | |
| PRAI | KR 1999-57483 | A | 19991214 | | |
| | WO 2000-KR1314 | W | 20001116 | | |
| OS | CASREACT 135:61459 | | | | |
| AB | <p>Disclosed is a method for prepg. DL-.alpha.-tocopherol through the condensation of isophytol or phytol derivs. and trimethylhydroquinone(TMHQ) using a catalyst system comprising a divalent metal halogen compd., silica gel and/or silica-alumina, and a Bronsted acid. Isophytol or phytol derivs. are slowly added to trimethylhydroquinone for the condensation thereof at 80 to 135 .degree.C over 30 to 60 min in the presence of the metal halogen and the silica gel and/or silica-alumina. In the presence of the Bronsted acid, the intermediates are converted into the product. The silica gel and/or silica-alumina is washed with a polar solvent for recovery. The catalyst system can remarkably reduce side-reactions upon the condensation of isophytol or phytol derivs. and TMHQ, thus producing DL-.alpha.-tocopherol with a high purity at a high yield. Also, the catalyst system can be regenerated in succession because of its being able to avoid the decrease of catalytic activity attributed to the adsorption of org. materials; thus reducing the prodn. cost of DL-.alpha.-tocopherol and the quantity of industrial wastes generated. With these advantages, the catalyst system can be effectively used in prepg. highly pure DL-.alpha.-tocopherol at a high yield on a com. scale.</p> | | | | |
| ST | DL alpha tocopherol synthesis; cyclocondensation isophytol trimethylhydroquinone metal halide catalyzed | | | | |
| IT | <p>Cyclocondensation reaction catalysts (divalent metal halide catalyst in cyclocondensation of isophytol and trimethylhydroquinone in prepn. of DL-alpha-tocopherol)</p> | | | | |
| IT | <p>Chlorides, uses Fluorides, uses Iodides, uses RL: CAT (Catalyst use); USES (Uses) (divalent; prepn. of DL-.alpha.-tocopherol with high yield and high purity)</p> | | | | |
| IT | <p>Alcohols, preparation Diterpenes RL: SPN (Synthetic preparation); PREP (Preparation) (hydroxy diterpenes; prepn. of DL-.alpha.-tocopherol with high yield and high purity)</p> | | | | |
| IT | <p>Cyclocondensation reaction (prepn. of DL-.alpha.-tocopherol with high yield and high purity)</p> | | | | |
| IT | <p>Silica gel, uses RL: CAT (Catalyst use); USES (Uses) (prepn. of DL-.alpha.-tocopherol with high yield and high purity)</p> | | | | |
| IT | <p>1344-28-1, Alumina, uses 7646-85-7, Zinc dichloride, uses 15438-31-0D, Iron dication, halide, uses 22541-90-8D, Tin dication, halide, uses</p> | | | | |

23713-49-7D, Zinc dication, halide, uses
 RL: CAT (Catalyst use); USES (Uses)
 (prepn. of DL-.alpha.-tocopherol with high yield and high purity)

IT 10191-41-0P, dl-.alpha.-Tocopherol
 RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. of DL-.alpha.-tocopherol with high yield and high purity)

IT 64-17-5, Ethanol, uses 67-56-1, Methanol, uses 67-63-0, Isopropyl alcohol, uses 67-64-1, Acetone, uses 71-23-8, Propanol, uses 71-36-3, Butanol, uses 71-41-0, Pentanol, uses 71-43-2, Benzene, uses 75-09-2, Dichloromethane, uses 78-93-3, Methyl ethyl ketone, uses 79-20-9, Methyl acetate 96-22-0, Diethyl ketone 105-53-3, Diethyl malonate 108-88-3, Toluene, uses 109-60-4, Propyl acetate 110-54-3, n-Hexane, uses 111-27-3, Hexanol, uses 111-65-9, n-Octane, uses 111-70-6, 1-Heptanol 111-87-5, Octanol, uses 123-86-4, Butyl acetate 124-18-5, n-Decane 141-78-6, Ethyl acetate, uses 142-82-5, n-Heptane, uses 563-80-4, Methyl isopropyl ketone 628-63-7, Pentyl acetate 1300-21-6, Dichloroethane 1330-20-7, Xylene, uses 26635-64-3, Isooctane 31394-54-4, Isoheptane 34464-38-5, Isodecane 43133-95-5, Methylpentane
 RL: NUU (Other use, unclassified); USES (Uses)
 (prepn. of DL-.alpha.-tocopherol with high yield and high purity)

IT 150-86-7D, Phytol, derivs. 505-32-8, Isophytol 700-13-0, Trimethylhydroquinone
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (prepn. of DL-.alpha.-tocopherol with high yield and high purity)

IT 104-15-4P, p-Toluenesulfonic acid, preparation 7647-01-0P, Hydrochloric acid, preparation 7664-38-2P, Phosphoric acid, preparation 7664-93-9P, Sulfuric acid, preparation 7697-37-2P, Nitric acid, preparation
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (prepn. of DL-.alpha.-tocopherol with high yield and high purity)

RE.CNT 4 THERE ARE 4 CITED REFERENCES AVAILABLE FOR THIS RECORD

RE

(1) Basf Ag; US 5468883 A 1995 HCPLUS
 (2) Kuraray Co; US 4252726 A 1981 HCPLUS
 (3) Mitsui Toatsu Chem Inc; JP 59190987 A 1984 HCPLUS
 (4) Nissin Flour Milling Co Ltd; JP 53-44570 A 1978 HCPLUS

L25 ANSWER 6 OF 23 HCPLUS COPYRIGHT 2003 ACS
 AN 2000:360971 HCPLUS
 DN 133:150747
 TI Synthesis of d,l-.alpha.-tocopherol using 'microencapsulated' catalysts
 AU Schager, F.; Bonrath, W.
 CS Vitamin Research and Technology Development, F. Hoffmann-La Roche Ltd., Basel, CH-4070, Switz.
 SO Applied Catalysis, A: General (2000), 202(1), 117-120
 CODEN: ACAGE4; ISSN: 0926-860X
 PB Elsevier Science B.V.
 DT Journal
 LA English
 CC 30-30 (Terpenes and Terpenoids)
 Section cross-reference(s): 67
 OS CASREACT 133:150747
 AB The synthesis of d,l-.alpha.-tocopherol starting from trimethylhydroquinone and isophytol using 'microencapsulated' catalysts, e.g. MC-(CF₃SO₂)₂NH, is described. Scope and limitations of this type of catalysts are discussed. Advantages of this new procedure are high yield and selectivity, no waste problem and mild reaction conditions. Best results in the synthesis of d,l-.alpha.-tocopherol using MC-catalysts are obtained in polar solvents. The used catalyst could not

be recovered.

- ST tocopherol alpha prepn microencapsulated catalyst
 IT Cyclocondensation reaction catalysts
 (synthesis of d,l-.alpha.-tocopherol using 'microencapsulated' catalysts)
 IT 82113-65-3 144026-79-9, Scandium triflate
 RL: CAT (Catalyst use); USES (Uses)
 (microencapsulated; synthesis of d,l-.alpha.-tocopherol using 'microencapsulated' catalysts)
 IT 505-32-8, Isophytol 700-13-0, Trimethylhydroquinone
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (synthesis of d,l-.alpha.-tocopherol using 'microencapsulated' catalysts)
 IT 10191-41-0P, (.+-.)-.alpha.-Tocopherol
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (synthesis of d,l-.alpha.-tocopherol using 'microencapsulated' catalysts)

RE.CNT 15 THERE ARE 15 CITED REFERENCES AVAILABLE FOR THIS RECORD

RE

- (1) Baak, M; WO 9821197 1996 HCPLUS
- (2) Baldenius, K; Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition 1996, VA27, P478
- (3) Finn, J; EP 100471 1982 HCPLUS
- (4) Greenbaum, S; US 3708505 1971 HCPLUS
- (5) Isler, O; Vitamine II 1988, P126
- (6) Karrer, P; US 2411967 1946 HCPLUS
- (7) Kobayashi, S; J Am Chem Soc 1998, V120, P2985 HCPLUS
- (8) March, J; Advanced Organic Chemistry, 3rd Edition 1985, P902
- (9) Matsui, M; EP 658552 A1 1993 HCPLUS
- (10) Matsui, M; Bull Chem Soc Jpn 1995, V68, P3569 HCPLUS
- (11) Nagayama, S; J Org Chem 1998, V63, P6094 HCPLUS
- (12) Nelan, D; US 3444213 1969 HCPLUS
- (13) Schager, F; J Catal 1999, V182, P284
- (14) Schulz, B; DE 3203487 1983 HCPLUS
- (15) Skoda, A; CS 254402 1989

L25 ANSWER 7 OF 23 HCPLUS COPYRIGHT 2003 ACS

AN 2000:335071 HCPLUS

DN 132:334646

TI Process for manufacturing d,l-.alpha.-tocopherol

IN Bonrath, Werner; Wang, Shaoning

PA F. Hoffmann-La Roche A.-G., Switz.

SO Eur. Pat. Appl., 8 pp.

CODEN: EPXXDW

DT Patent

LA English

IC ICM C07D311-72

CC 30-20 (Terpenes and Terpenoids)

FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|----|--|------|----------|-----------------|----------|
| PI | EP 1000940 | A1 | 20000517 | EP 1999-121898 | 19991105 |
| | R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO | | | | |
| | KR 2000035335 | A | 20000626 | KR 1999-49441 | 19991109 |
| | CN 1253950 | A | 20000524 | CN 1999-123521 | 19991110 |
| | JP 2000143656 | A2 | 20000526 | JP 1999-319283 | 19991110 |
| | BR 9905319 | A | 20010417 | BR 1999-5319 | 19991110 |
| | US 2002010347 | A1 | 20020124 | US 2001-932519 | 20010817 |
| | US 6423851 | B2 | 20020723 | | |

PRAI EP 1998-121457 A 19981111
 US 1999-438711 B1 19991111
 OS CASREACT 132:334646

AB The manuf. of d,l-.alpha.-tocopherol by the catalyzed condensation of trimethylhydroquinone with **isophytol** comprises carrying out the condensation in the presence of bis-(trifluoromethylsulfonyl)amine, or a metal salt thereof of formula M[N(SO₂CF₃)₂]_n [M = metal; n = 1-4], in supercrit. carbon dioxide or nitrous oxide as the solvent. Thus, trimethylhydroquinone, **isophytol** and bis(trifluoromethanesulfonyl)amine in supercrit. carbon dioxide were mixed in a stainless steel autoclave and heated to 150.degree.C at 85 bar to give dl-.alpha.-tocopherol in 84.23% yield.

ST tocopherol prepn condensation trifluoromethylsulfonylamine catalyst

IT Condensation reaction

Condensation reaction catalysts
 (prep. of d,l-.alpha.-tocopherol via trifluoromethanesulfonylamine catalyzed condensation)

IT 64-17-5, Ethanol, uses 67-56-1, Methanol, uses 67-64-1, Acetone, uses 74-98-6, Propane, uses 96-22-0, Diethyl ketone 108-10-1, Isobutyl methyl ketone
 RL: NUU (Other use, unclassified); USES (Uses)
 (cosolvent; prep. of d,l-.alpha.-tocopherol via trifluoromethanesulfonylamine catalyzed condensation)

IT 82113-65-3, Bis(trifluoromethylsulfonyl)amine 189114-61-2, Silver bis(trifluoromethanesulfonyl)amide
 RL: CAT (Catalyst use); USES (Uses)
 (prep. of d,l-.alpha.-tocopherol via trifluoromethanesulfonylamine catalyzed condensation)

IT 10191-41-0P, dl-.alpha.-Tocopherol
 RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
 (prep. of d,l-.alpha.-tocopherol via trifluoromethanesulfonylamine catalyzed condensation)

IT 505-32-8, Isophytol 700-13-0, Trimethylhydroquinone
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (prep. of d,l-.alpha.-tocopherol via trifluoromethanesulfonylamine catalyzed condensation)

IT 124-38-9, Carbon dioxide, uses 10024-97-2, Nitrous oxide, uses
 RL: NUU (Other use, unclassified); USES (Uses)
 (solvent; prep. of d,l-.alpha.-tocopherol via trifluoromethanesulfonylamine catalyzed condensation)

RE.CNT 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD
 RE

- (1) Anon; PATENT ABSTRACTS OF JAPAN 1985, V009(309)
- (2) Eisai Co Ltd; EP 0658552 A 1995 HCPLUS
- (3) F Hoffmann-La Roche Ag; WO 9821197 A 1998 HCPLUS
- (4) Ishihara, K; SYNLETT 11, P1045 HCPLUS
- (5) Mitsui Petrochem Ind K K; JP 60149582 A 1985 HCPLUS

L25 ANSWER 8 OF 23 HCPLUS COPYRIGHT 2003 ACS

AN 2000:256793 HCPLUS

DN 133:30610

TI The synthesis of D,L-.alpha.-tocopherol in supercritical media
 AU Wang, Shaoning; Bonrath, Werner; Pauling, Horst; Kienzle, Frank
 CS F. Hoffmann-La Roche Ltd., Basel, Switz.
 SO Journal of Supercritical Fluids (2000), 17(2), 135-143
 CODEN: JSFLEH; ISSN: 0896-8446

PB Elsevier Science B.V.

DT Journal

LA English

CC 26-8 (Biomolecules and Their Synthetic Analogs)
 OS CASREACT 133:30610
 AB The synthesis of D,L-.alpha.-tocopherol in supercrit. carbon dioxide or nitrous oxide by condensation of trimethylhydroquinone (TMHQ) with **isophytol** (IP) in the presence of various Bronsted or Lewis acids, esp. an imide or its metal salts, as catalysts is described. The product is obtained in high yield. The method represents an interesting alternative to existing processes. A quasi-reaction mechanism is being proposed together with kinetics, which are needed for the reactor anal. and design.
 ST Bronsted Lewis acid cyclocondensation trimethylhydroquinone **isophytol**; tocopherol prepn Bronsted Lewis acid cyclocondensation; vitamin E prepn Bronsted Lewis cyclocondensation
 IT Cyclocondensation reaction
 Cyclocondensation reaction catalysts
 (prepns. of D,L-.alpha.-tocopherol in supercrit. media)
 IT Bronsted acids
 Lewis acids
 RL: **CAT (Catalyst use); USES (Uses)**
 (prepns. of D,L-.alpha.-tocopherol in supercrit. media)
 IT 1343-93-7, 12-Tungstophosphoric acid (H3PW12O40) 9037-24-5, Amberlyst-15
 82113-65-3, Bis(trifluoromethanesulfonyl)amine 90076-65-6, Lithium bis(trifluoromethylsulfonyl)amide 118473-68-0, Nafion NR50
 189114-61-2, Silver bis(trifluoromethylsulfonyl)amide
 RL: **CAT (Catalyst use); USES (Uses)**
 (prepns. of D,L-.alpha.-tocopherol in supercrit. media)
 IT 124-38-9, Carbon dioxide, uses 10024-97-2, Nitrogen oxide (N₂O), uses
 RL: NUU (Other use, unclassified); USES (Uses)
 (prepns. of D,L-.alpha.-tocopherol in supercrit. media)
 IT 505-32-8, **Isophytol** 700-13-0, Trimethylhydroquinone
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (prepns. of D,L-.alpha.-tocopherol in supercrit. media)
 IT 10191-41-0P, D,L-.alpha.-Tocopherol
 RL: **SPN (Synthetic preparation); PREP (Preparation)**
 (prepns. of D,L-.alpha.-tocopherol in supercrit. media)
 RE.CNT 13 THERE ARE 13 CITED REFERENCES AVAILABLE FOR THIS RECORD
 RE
 (1) Anon; Chemical Market Reporter 1997, P5
 (2) Baldenius, K; Ullmann's Encyclopedia of Industrial Chemistry 1996, VA27, P484
 (3) Bonrath, W; European Patent Application 1998
 (4) Brunner, G; J Supercritical Fluids 1991, V4, P72 HCPLUS
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 L25 ANSWER 9 OF 23 HCPLUS COPYRIGHT 2003 ACS
 AN 2000:136771 HCPLUS
 DN 132:222678
 TI Catalyzed synthesis of DL-.alpha.-tocopherol by phosphomolybdic acid
 AU Qian, Dong; Yao, Li-Min; Tan, Yan-Zhi; Cui, Jia
 CS School of Chemistry and Chemical Engineering, Central South University of Technology, Changsha, 410083, Peop. Rep. China

SO Hecheng Huaxue (1999), 7(4), 401-402
 CODEN: HEHUE2; ISSN: 1005-1511
 PB Hecheng Huaxue Bianjibu
 DT Journal
 LA Chinese
 CC 30-30 (Terpenes and Terpenoids)
 AB DL-.alpha.-Tocopherol was synthesized by condensing 2,3
 5-trimethylhydroquinone with **isophytol** at room temp. using
 phosphomolybdic acid (H3PMo12O40) as a catalyst. It was found that
 H3PMo12O40 was a high active catalyst for the synthesis of
 DL-.alpha.-tocopherol and could easily be sepd. and reused.
 ST tocopherol prepn; **isophytol** condensation catalyst
 methylhydroquinone phosphomolybdic acid
 IT Condensation reaction catalysts
 (catalyzed synthesis of DL-.alpha.-tocopherol by phosphomolybdic acid)
 IT 12026-57-2, Phosphomolybdic acid (H3PMo12O40)
 RL: **CAT (Catalyst use); USES (Uses)**
 (catalyzed synthesis of DL-.alpha.-tocopherol by phosphomolybdic acid)
 IT 505-32-8, **Isophytol 700-13-0**, 2,3 5-
 Trimethylhydroquinone
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (catalyzed synthesis of DL-.alpha.-tocopherol by phosphomolybdic acid)
 IT 10191-41-0P, DL-.alpha.-Tocopherol
 RL: **SPN (Synthetic preparation); PREP (Preparation)**
 (catalyzed synthesis of DL-.alpha.-tocopherol by phosphomolybdic acid)

L25 ANSWER 10 OF 23 HCPLUS COPYRIGHT 2003 ACS
 AN 2000:76974 HCPLUS

DN 132:122784

TI Process for the preparation of .alpha.-tocopherol

IN Hirose, Noriyasu; Inoue, Hiroshi; Matsunami, Toshio; Yoshimura, Takashi;
 Morita, Kouzou; Horikawa, Yuh; Iwata, Noriyoshi; Minami, Norio; Hayashi,
 Kenji; Seki, Chiaki

PA Eisai Co., Ltd., Japan

SO U.S., 7 pp., Cont.-in-part of U.S. 5,886,197.

CODEN: USXXAM

DT Patent

LA English

IC ICM C07D311-20

NCL 549411000

CC 30-20 (Terpenes and Terpenoids)

FAN.CNT 2

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|----|-------------|------|----------|-----------------|----------|
| PI | US 6020505 | A | 20000201 | US 1998-210663 | 19981214 |
| | US 5663376 | A | 19970902 | US 1995-460667 | 19950602 |
| | JP 09188673 | A2 | 19970722 | JP 1997-15371 | 19950727 |
| | JP 09188674 | A2 | 19970722 | JP 1997-15372 | 19950727 |
| | US 5886197 | A | 19990323 | US 1997-826504 | 19970403 |

PRAI JP 1994-175167 A 19940727

JP 1994-282309 A 19941116

US 1995-460667 A3 19950602

US 1997-826504 A2 19970403

JP 1995-191719 A3 19950727

OS CASREACT 132:122784; MARPAT 132:122784

AB A process for the prepn. of .alpha.-tocopherol via cyclocondensation
 reaction of trimethylhydroquinone and a specific **phytol** deriv.
 or **isophytol** was presented. The cyclocondensation reaction was
 conducted in various solvents, such as a carbonate ester, a lower fatty
 acid ester R₁COOR₂ (R₁, R₂ = alkyl), a mixed solvent of a nonpolar solvent

and an alc., or a mixed solvent of a nonpolar solvent and a lower fatty acid ester. Thus, (.-+.-)-.alpha.-tocopherol was prep'd in 98.6% yield by cyclocondensation of 2,3,5-trimethylhydroquinone and **isophytol** using hydrochloric acid and zinc chloride as a catalyst and iso-Bu acetate as the solvent. (.-+.-)-.alpha.-Tocopherol was similarly prep'd in 95.9% using in a hexane and 1-butanol mixed solvent system and in 99.1% yield using hydrobromic acid and zinc bromide in di-Et acetate.

ST tocopherol prep'n cyclocondensation
IT Cyclocondensation reaction

(process for the prepn. of .alpha.-tocopherol via cyclocondensation reaction of trimethylhydroquinone a **phytol** deriv. or **isophytol**)

IT Ligoine

RL: NUU (Other use, unclassified); USES (Uses)
(process for the prepn. of .alpha.-tocopherol via cyclocondensation reaction of trimethylhydroquinone a **phytol** deriv. or **isophytol**)

IT 7646-85-7, Zinc chloride, uses 7699-45-8, Zinc bromide

RL: CAT (Catalyst use); USES (Uses)
(process for the prepn. of .alpha.-tocopherol via cyclocondensation reaction of trimethylhydroquinone a **phytol** deriv. or **isophytol**)

IT 10191-41-0P, (.-+.-)-.alpha.-Tocopherol

RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)

(process for the prepn. of .alpha.-tocopherol via cyclocondensation reaction of trimethylhydroquinone a **phytol** deriv. or **isophytol**)

IT 71-23-8, 1-Propanol, uses 71-36-3, 1-Butanol, uses 71-41-0,
1-Pentanol, uses 75-85-4, tert-Amyl alcohol 96-49-1, Ethylene carbonate 97-62-1, Ethyl isobutyrate 105-54-4, Ethyl butyrate 105-58-8, Diethyl carbonate 108-21-4, 2-Propyl acetate 108-32-7, Propylene carbonate 108-64-5, Ethyl isovalerate 108-88-3, Toluene, uses 109-60-4, 1-Propyl acetate 110-19-0, Isobutyl acetate 110-54-3, Hexane, uses 110-82-7, Cyclohexane, uses 123-86-4, 1-Butyl acetate 142-82-5, Heptane, uses 547-63-7, Methyl isobutyrate 590-01-2 616-38-6, Dimethyl carbonate 623-53-0, Methyl ethyl carbonate 624-24-8, Methyl valerate 638-11-9, Butanoic acid 1-methylethyl ester 3938-95-2, Ethyl pivalate

RL: NUU (Other use, unclassified); USES (Uses)
(process for the prepn. of .alpha.-tocopherol via cyclocondensation reaction of trimethylhydroquinone a **phytol** deriv. or **isophytol**)

IT 505-32-8, **Isophytol** 700-13-0, 2,3,5-

Trimethylhydroquinone 7647-01-0, Hydrochloric acid, reactions 10035-10-6, Hydrobromic acid, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)

(process for the prepn. of .alpha.-tocopherol via cyclocondensation reaction of trimethylhydroquinone a **phytol** deriv. or **isophytol**)

RE.CNT 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD

RE

- (1) Hirose; US 5663376 1997 HCPLUS
- (2) Hirose; US 5886197 1999 HCPLUS

L25 ANSWER 11 OF 23 HCPLUS COPYRIGHT 2003 ACS

AN 2000:34868 HCPLUS

DN 132:78721

TI Method of producing vitamin E

IN Hyatt, John Anthony

PA Eastman Chemical Company, USA
 SO PCT Int. Appl., 38 pp.
 CODEN: PIXXD2
 DT Patent
 LA English
 IC ICM C07D311-72
 ICS C07D303-16; C07C069-145; C07C043-166
 CC 30-20 (Terpenes and Terpenoids)
 FAN.CNT 3

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|---|------|----------|-----------------|----------|
| PI | WO 2000001686 | A1 | 20000113 | WO 1999-US14976 | 19990701 |
| | W: BR, CN, JP, MX | | | | |
| | RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE | | | | |
| | WO 2000001685 | A1 | 20000113 | WO 1999-US14975 | 19990701 |
| | W: CN, JP | | | | |
| | RW: AT, BH, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SH | | | | |
| | BR 9911873 | A | 20010327 | BR 1999-11873 | 19990701 |
| | EP 1095033 | A1 | 20010502 | EP 1999-933650 | 19990701 |
| | R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO | | | | |
| | EP 1095034 | A1 | 20010502 | EP 1999-935390 | 19990701 |
| | R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, FI | | | | |
| | JP 2002519416 | T2 | 20020702 | JP 2000-558089 | 19990701 |
| | JP 2002519417 | T2 | 20020702 | JP 2000-558090 | 19990701 |
| | US 6156913 | A | 20001205 | US 1999-347769 | 19990706 |
| | US 6242227 | B1 | 20010605 | US 1999-352654 | 19990706 |
| | US 6262279 | B1 | 20010717 | US 1999-348192 | 19990706 |
| | US 6410755 | B1 | 20020625 | US 1999-348097 | 19990706 |
| PRAI | US 1998-91868P | P | 19980706 | | |
| | US 1998-91983P | P | 19980706 | | |
| | WO 1999-US14975 | W | 19990701 | | |
| | WO 1999-US14976 | W | 19990701 | | |
| OS | CASREACT 132:78721; MARPAT 132:78721 | | | | |
| AB | The invention provides processes for producing phytol , isophytol , and certain phytol derivs. by a method of oxidizing or epoxidizing geranylgeraniol or geranylgeraniol derivs. to form epoxygeranylgeraniol derivs., reducing or hydrogenating the epoxygeranylgeraniol derivs. to produce epoxyphytol derivs., and then deoxygenating the epoxyphytol derivs. to produce phytol , isophytol , phytene derivs., isophytene derivs., or mixts. thereof. The step of deoxygenating is carried out in the presence of deoxygenation catalysts, including rhenium trioxide compds. The invention also provides methods for the synthesis of certain novel substituted epoxyphytol compds. and substituted phytene compds. having removable protecting groups. The produced phytol , isophytol , phytene derivs., isophytene derivs., substituted epoxyphytol compds. and substituted phytene compds. are suitable starting materials for condensation with trimethylhydroquinone derivs. in the presence of Lewis acids to give tocopherol derivs. including .alpha.-tocopherol, vitamin E. Thus, geranylgeraniol is epoxidized using vanadium tris(acetylacetone) and tert-butylhydroperoxide to give 2,3-epoxygeranylgeraniol in 98% yield. 2,3-Epoxygeranylgeraniol is hydrogenated with Pd/C, and the resulting 2,3- epoxyphytol is deoxygenated with methylrhenium trioxide to give a mixt. of isophytol and phytol in 90% yield. | | | | |
| ST | vitamin E prepn; tocopherol prepn; phytol prepn tocopherol | | | | |

IT intermediate; **isophytol** prepn tocopherol intermediate
 IT Epoxidation
 Reduction
 (pregn. of **phytol** and **isophytol** as tocopherol
 intermediates)
 IT Tocopherols
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (pregn. of **phytol** and **isophytol** as tocopherol
 intermediates)
 IT 70197-13-6, Methylrhenium trioxide
 RL: **CAT (Catalyst use)**; USES (Uses)
 (deoxygenation catalyst; pregn. of **phytol** and
 isophytol as tocopherol intermediates)
 IT 13476-99-8, Vanadium tris(acetylacetone)
 RL: **CAT (Catalyst use)**; USES (Uses)
 (epoxidn. catalyst; pregn. of **phytol** and **isophytol**
 as tocopherol intermediates)
 IT 7440-05-3, Palladium, uses
 RL: **CAT (Catalyst use)**; USES (Uses)
 (hydrogenation catalyst; pregn. of **phytol** and
 isophytol as tocopherol intermediates)
 IT 505-32-8P, **Isophytol** 106938-96-9P 107438-44-8P
 221234-74-8P, 2,3-Epoxygeranylgeraniol 253686-88-3P, **dl-Phytol**
 253686-93-0P
 RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic
 preparation); PREP (Preparation); RACT (Reactant or reagent)
 (pregn. of **phytol** and **isophytol** as tocopherol
 intermediates)
 IT 10191-41-0P, **dl-.alpha.-Tocopherol**
 RL: IMF (Industrial manufacture); SPN (Synthetic
 preparation); PREP (Preparation)
 (pregn. of **phytol** and **isophytol** as tocopherol
 intermediates)
 IT 75-91-2, **tert-Butylhydroperoxide** 80-15-9, **Cumene hydroperoxide**
 700-13-0, **Trimethylhydroquinone** 7722-84-1, **Hydrogen peroxide**,
 reactions 24034-73-9
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (pregn. of **phytol** and **isophytol** as tocopherol
 intermediates)

RE.CNT 4 THERE ARE 4 CITED REFERENCES AVAILABLE FOR THIS RECORD

RE

- (1) Anon; 1989, 30, P687 HCAPLUS
- (2) Eisai; JP 62209072 A 1987 HCAPLUS
- (3) Stalla-Bourdillon, B; IND CHIM BEL 1970, V35(1), P13 HCAPLUS
- (4) Teijin; DE 2404621 A 1975 HCAPLUS

L25 ANSWER 12 OF 23 HCAPLUS COPYRIGHT 2003 ACS

AN 2000:34593 HCAPLUS

DN 132:78720

TI Manufacture of **d,l-.alpha.-tocopherol**

IN Aquino, Fabrice; Bonrath, Werner

PA F. Hoffmann-La Roche AG, Switz.

SO Eur. Pat. Appl., 9 pp.

CODEN: EPXXDW

DT Patent

LA English

IC ICM C07D311-72

CC 30-20 (Terpenes and Terpenoids)

FAN.CNT 1

PATENT NO.

KIND DATE

APPLICATION NO. DATE

| PI | EP 970953 | A1 | 20000112 | EP 1999-112324 | 19990626 |
|------|---|------------|----------|-------------------------|-------------------------|
| | R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO | US 6452023 | B1 | 20020917 | US 1999-342272 19990629 |
| | KR 2000011530 | A | 20000225 | KR 1999-27181 19990707 | |
| | JP 2000044556 | A2 | 20000215 | JP 1999-194076 19990708 | |
| | BR 9902781 | A | 20000516 | BR 1999-2781 19990708 | |
| | CN 1241566 | A | 20000119 | CN 1999-110422 19990709 | |
| PRAI | EP 1998-112842 | A | 19980710 | | |
| OS | CASREACT 132:78720 | | | | |

AB dl-.alpha.-Tocopherol is prep'd. by the condensation of trimethylhydroquinone and **isophytol** or **phytol** in the presence of a catalyst that is non-toxic and has no corrosive action. Thus, 2,3,5-trimethylhydroquinone and **isophytol** are reacted in the presence of 12-tungstophosphoric acid in hexane to give dl-.alpha.-tocopherol in 97% yield and 91.4% purity.

ST tocopherol prepn

IT Condensation reaction
(prepn. of dl-.alpha.-tocopherol)

IT Condensation reaction catalysts

Corrosion prevention
(prepn. of dl-.alpha.-tocopherol using a catalyst that is non-toxic and has no corrosive action)

IT 1343-93-7, 12-Tungstophosphoric acid 12026-57-2, 12-Molybdophosphoric acid 12027-38-2, 12-Tungstosilicic acid

RL: CAT (Catalyst use); USES (Uses)
(prepn. of dl-.alpha.-tocopherol)

IT 10191-41-0P, dl-.alpha.-Tocopherol
RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
(prepn. of dl-.alpha.-tocopherol)

IT 150-86-7, **Phytol** 505-32-8, **Isophytol**
700-13-0, 2,3,5-Trimethylhydroquinone
RL: RCT (Reactant); RACT (Reactant or reagent)
(prepn. of dl-.alpha.-tocopherol)

IT 96-49-1, Ethylene carbonate 108-32-7, Propylene carbonate 110-54-3, Hexane, uses 111-65-9, Octane, uses 142-82-5, Heptane, uses
RL: NUU (Other use, unclassified); USES (Uses)
(solvent; prepn. of dl-.alpha.-tocopherol)

RE.CNT 14 THERE ARE 14 CITED REFERENCES AVAILABLE FOR THIS RECORD

RE

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- (2) Anon; CA 2154605 A 1996 HCPLUS
- (3) Anon; EP 694541 A 1996 HCPLUS
- (4) Anon; JP 8193079 A 1996
- (5) Anon; DE 19603142 A 1997 HCPLUS
- (6) Anon; DE 19617444 A 1997 HCPLUS
- (7) Anon; JP 2644460 B 1997 HCPLUS
- (8) Anon; US 5663376 A 1997 HCPLUS
- (9) Anon; JP 9188673 A 1997
- (10) Anon; JP 9188674 A 1997
- (11) Anon; WO 9728151 A 1997 HCPLUS
- (12) Anon; EP 0882036 A 1998 HCPLUS
- (13) Anon; CN 1211243 A 1999 HCPLUS
- (14) Anon; US 5886197 A 1999 HCPLUS

L25 ANSWER 13 OF 23 HCPLUS COPYRIGHT 2003 ACS
AN 1999:659082 HCPLUS
DN 131:272041

TI Process for manufacturing D,L-.alpha.-tocopherol in a carbonate solvent
 and in the presence of a sulfur-containing acid catalyst
 IN Baak, Marcel; Bonrath, Werner; Kreienbuehl, Paul
 PA F. Hoffmann-La Roche A.-G., Switz.
 SO Eur. Pat. Appl., 8 pp.
 CODEN: EPXXDW
 DT Patent
 LA English
 IC ICM C07D311-72
 CC 30-20 (Terpenes and Terpenoids)
 FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|--|------|----------|-----------------|----------|
| PI | EP 949255 | A1 | 19991013 | EP 1999-106507 | 19990330 |
| | R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO | | | | |
| | US 6066745 | A | 20000523 | US 1999-282411 | 19990331 |
| | CN 1234402 | A | 19991110 | CN 1999-104919 | 19990406 |
| | JP 2000053673 | A2 | 20000222 | JP 1999-98266 | 19990406 |
| PRAI | EP 1998-106237 | A | 19980406 | | |
| OS | CASREACT 131:272041 | | | | |

AB A process for the manuf. of D,L-.alpha.-tocopherol by acid-catalyzed condensation of trimethylhydroquinone with **isophytol** comprises carrying out the condensation in the presence of sulfuric acid, methanesulfonic acid, ethanesulfonic acid, trifluoromethanesulfonic acid, p-toluenesulfonic acid, or fluorosulfonic acid (in concn. of .1toreq. 0.4 wt.% based on the wt. of **isophytol**) in ethylene or propylene carbonate or a mixt. of both carbonates, or in a mixt. of one or both of the carbonates and a non-polar solvent. Thus, 2,3,5-trimethylhydroquinone was condensed with **isophytol** in ethylene carbonate-heptane contg. 10% vol./vol. H₂SO₄ to give 94.1% D,L-.alpha.-tocopherol.

ST tocopherol prep; methylhydroquinone cycloaddn **isophytol**; catalyst acid methylhydroquinone cycloaddn **isophytol**; solvent carbonate methylhydroquinone cycloaddn **isophytol**

IT Cycloaddition reaction catalysts
 (acids; process for manufg. D,L-tocopherol in a carbonate solvent and in presence of a sulfur-contg. acid catalyst)

IT Carbonates, uses

RL: NUU (Other use, unclassified); USES (Uses)
 (as solvents; for cycloaddn. reaction of trimethylhydroquinone with **isophytol** in prepn. of .alpha.-tocopherol)

IT Solvents

(carbonates; for cycloaddn. reaction of trimethylhydroquinone with **isophytol** in prepn. of .alpha.-tocopherol)

IT Cycloaddition reaction

(process for manufg. D,L-tocopherol in a carbonate solvent and in presence of a sulfur-contg. acid catalyst)

IT Acids, uses

RL: CAT (Catalyst use); USES (Uses)
 (process for manufg. D,L-tocopherol in a carbonate solvent and in presence of a sulfur-contg. acid catalyst)

IT 75-75-2, Methanesulfonic acid 104-15-4, p-Toluenesulfonic acid, uses 594-45-6, Ethanesulfonic acid 1493-13-6, Trifluoromethanesulfonic acid 7664-93-9, Sulfuric acid, uses 7789-21-1, Fluorosulfonic acid

RL: CAT (Catalyst use); USES (Uses)
 (process for manufg. D,L-tocopherol in a carbonate solvent and in presence of a sulfur-contg. acid catalyst)

IT 96-49-1, Ethylene carbonate 108-32-7, Propylene carbonate

RL: NUU (Other use, unclassified); USES (Uses)
 (process for manufg. D,L-tocopherol in a carbonate solvent and in

presence of a sulfur-contg. acid catalyst)
IT 505-32-8, **Isophytol 700-13-0**, Trimethylhydroquinone
RL: RCT (Reactant); RACT (Reactant or reagent)
(process for manufg. D,L-tocopherol in a carbonate solvent and in
presence of a sulfur-contg. acid catalyst)
IT **10191-41-0P**, (.+-.)-.alpha.-Tocopherol
RL: **SPN (Synthetic preparation); PREP (Preparation)**
(process for manufg. D,L-tocopherol in a carbonate solvent and in
presence of a sulfur-contg. acid catalyst)

RE.CNT 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD

RE

- (1) Basf Aktiengesellschaft; WO 9728151 A 1997 HCPLUS
- (2) Eisai Co Ltd; EP 0694541 A 1996 HCPLUS
- (3) Greenbaum, S; US 3708505 A 1973 HCPLUS
- (4) Kajiwara, M; HETEROCYCLES 1981, V15(2), P1209 HCPLUS
- (5) Urano, S; HETEROCYCLES 1984, V22(9), P1975 HCPLUS

L25 ANSWER 14 OF 23 HCPLUS COPYRIGHT 2003 ACS

AN 1999:119233 HCPLUS

DN 130:282189

TI Synthesis of D,L-.alpha.-Tocopherol Using Strong Solid Acids as Catalysts

AU Schager, Frank; Bonrath, Werner

CS Vitamin Research and Technology Development, F. Hoffmann-La Roche Ltd.,
Basel, CH-4070, Switz.

SO Journal of Catalysis (1999), 182(1), 282-284

CODEN: JCTLA5; ISSN: 0021-9517

PB Academic Press

DT Journal

LA English

CC 30-20 (Terpenes and Terpenoids)

OS CASREACT 130:282189

AB The synthesis of DL-.alpha.-tocopherol starting from trimethylhydroquinone and **isophytol** using a heterogeneous solid acid catalyst, e.g., Nafion NR 50, is described. Advantages of this new procedure are high yield and selectivity, facile recovery of the catalyst, no waste problems, and mild reaction conditions. (c) 1999 Academic Press.

ST tocopherol synthesis solid acid catalyst Friedel Craft reaction

IT Friedel-Crafts reaction

Friedel-Crafts reaction catalysts

(synthesis of DL-.alpha.-tocopherol using strong solid acid catalysts)

IT Acids, uses

RL: **CAT (Catalyst use); USES (Uses)**

(synthesis of DL-.alpha.-tocopherol using strong solid acid catalysts)

IT 96-22-0, Diethyl ketone 96-48-0, .gamma.-Butyrolactone 108-10-1,
Isobutyl methyl ketone 108-32-7, Propylene carbonate 108-88-3,
Toluene, uses

RL: NUU (Other use, unclassified); USES (Uses)

(solvent; synthesis of DL-.alpha.-tocopherol using strong solid acid catalysts)

IT 9037-24-5, Amberlyst 15 118473-68-0, Nafion NR 50

RL: **CAT (Catalyst use); USES (Uses)**

(synthesis of DL-.alpha.-tocopherol using strong solid acid catalysts)

IT 505-32-8, **Isophytol 700-13-0**

RL: RCT (Reactant); RACT (Reactant or reagent)

(synthesis of DL-.alpha.-tocopherol using strong solid acid catalysts)

IT **10191-41-0P**, DL-.alpha.-Tocopherol

RL: **SPN (Synthetic preparation); PREP (Preparation)**

(synthesis of DL-.alpha.-tocopherol using strong solid acid catalysts)

RE.CNT 18 THERE ARE 18 CITED REFERENCES AVAILABLE FOR THIS RECORD
RE

- (1) Bonrath, W; EP 782993 1997 HCPLUS
- (2) Childs, R; J Org Chem 1982, V47, P4207
- (3) Finn, J; EP 100471 1982 HCPLUS
- (4) Greenbaum, S; US 3708505 1971 HCPLUS
- (5) Harmer, M; J Am Chem Soc 1996, V118, P7708 HCPLUS
- (6) Heidekum, A; J Catal 1998, V176, P260 HCPLUS
- (7) Isler, O; Vitamine I 1988, P126
- (8) Karrer, P; US 2411967 1946 HCPLUS
- (9) Matsui, M; Bull Chem Soc Jpn 1995, V68, P3569 HCPLUS
- (10) Nelan, D; US 3444213 1969 HCPLUS
- (11) Olah, G; J Org Chem 1977, V42, P4187 HCPLUS
- (12) Olah, G; Science 1979, V206, P13 HCPLUS
- (13) Olah, G; Synthesis 1978, P672 HCPLUS
- (14) Olah, G; Synthesis 1986, P513 HCPLUS
- (15) Schulz, B; DE 3203487 1983 HCPLUS
- (16) Skoda, A; CS 254402 1989
- (17) Tachibana, Y; Bull Chem Soc Jpn 1977, V50, P2477 HCPLUS
- (18) Waller, F; Chem Tech 1987, V17, P438 HCPLUS

L25 ANSWER 15 OF 23 HCPLUS COPYRIGHT 2003 ACS
AN 1998:341555 HCPLUS
DN 129:28106
TI Process for manufacturing d,l-.alpha.-tocopherol via catalyzed condensation
IN Baak, Marcel; Bonrath, Werner; Pauling, Horst
PA F. Hoffmann-La Roche A.-G., Switz.
SO PCT Int. Appl., 16 pp.
CODEN: PIXXD2
DT Patent
LA English
IC ICM C07D311-00
CC 30-20 (Terpenes and Terpenoids)
FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|---|-----------|----------|-----------------|----------|
| PI | WO 9821197 | A2 | 19980522 | WO 1997-EP6227 | 19971110 |
| | W: CN, JP, KR RW: AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE US 5908939 | A | 19990601 | US 1997-951273 | 19971016 |
| | EP 937055 | A2 | 19990825 | EP 1997-950150 | 19971110 |
| | EP 937055 | B1 | 20020403 | | |
| | R: BE, CH, DE, DK, ES, FR, GB, IT, LI, NL, SE, IE CN 1237163 | A | 19991201 | CN 1997-199633 | 19971110 |
| | JP 2001504111 | T2 | 20010327 | JP 1998-522153 | 19971110 |
| | ES 2173500 | T3 | 20021016 | ES 1997-950150 | 19971110 |
| | KR 2000053181 | A | 20000825 | KR 1999-704139 | 19990510 |
| PRAI | EP 1996-118037 | A | 19961111 | | |
| | WO 1997-EP6227 | W | 19971110 | | |
| OS | CASREACT | 129:28106 | | | |
| AB | A process for the manuf. of dl-.alpha.-tocopherol by the catalyzed condensation of trimethylhydroquinone with isophytol is described. The method comprises carrying out the condensation in the presence of bis-(trifluoromethylsulfonyl)amine [HN(SO ₂ CF ₃) ₂] or a metal salt thereof, of the formula M[N(SO ₂ CF ₃) ₂] _n (I) [M = metal atom selected from the group of lithium, boron, magnesium, aluminum, silicon, scandium, titanium, vanadium, manganese, iron, cobalt, nickel, copper, zinc, yttrium, zirconium, rhodium, palladium, silver, tin, lanthanum, cerium, neodymium, praseodymium, europium, dysprosium, ytterbium, hafnium, platinum and gold; n = the corresponding valency (1, 2, 3 or 4) of the metal atom M], as the catalyst, or of a combination of a metal salt of | | | | |

formula I and a strong Bronsted acid as the catalyst system in an org. solvent. Thus, a mixt. of trimethylhydroquinone, **isophytol** and bis-(trifluoromethylsulfonyl)amine in toluene are boiled at 140.degree.C to give dl-.alpha.-tocopherol in 90% yield.

ST tocopherol prepn catalyzed condensation

IT Condensation reaction

Condensation reaction catalysts

(prepn. of dl-.alpha.-tocopherol via catalyzed condensation)

IT 7440-16-6D, Rhodium, bis(trifluoromethylsulfonyl)amide complexes, uses 82113-65-3, Bis-(trifluoromethylsulfonyl)amine 82113-65-3D, rhodium complexes 90076-65-6, Lithium bis(trifluoromethylsulfonyl)amide 133395-16-1 162715-14-2 168106-25-0 168106-26-1 175438-45-6 176726-07-1 189114-61-2 189114-76-9 189114-86-1 207861-54-9 207861-55-0 207861-57-2 207861-59-4 207861-61-8 207861-63-0 207861-64-1 207861-65-2 207861-66-3 207861-67-4 207861-68-5 207861-69-6 207861-70-9 207861-71-0 207861-72-1

RL: **CAT (Catalyst use); USES (Uses)**

(prepn. of dl-.alpha.-tocopherol via catalyzed condensation)

IT 10191-41-0P, dl-.alpha.-Tocopherol

RL: **IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)**

(prepn. of dl-.alpha.-tocopherol via catalyzed condensation)

IT 505-32-8, **Isophytol** 700-13-0, Trimethylhydroquinone

RL: **RCT (Reactant); RACT (Reactant or reagent)**

(prepn. of dl-.alpha.-tocopherol via catalyzed condensation)

L25 ANSWER 16 OF 23 HCPLUS COPYRIGHT 2003 ACS

AN 1998:25397 HCPLUS

DN 128:154258

TI Preparation of .alpha.-tocopherol with scandium complex as recyclable catalyst

IN Yamamoto, Takashi

PA Eisai Co., Ltd., Japan; Central Glass Co., Ltd.

SO Jpn. Kokai Tokkyo Koho, 5 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

IC ICM C07D311-72

ICS B01J031-22; C07B061-00

CC 30-20 (Terpenes and Terpenoids)

FAN.CNT 1

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------------|------|-------|-----------------|-------|
| ----- | ---- | ----- | ----- | ----- |

PI JP 10001477 A2 19980106 JP 1996-171638 19960612

PRAI JP 1996-171638 19960612

OS CASREACT 128:154258

AB .alpha.-Tocopherol (I) is prep'd. by condensation of trimethylhydroquinone (II) with **phytol**, phytol halides, phytol acetate, phytol methanesulfonate, phytol ethanesulfonate, phytol benzenesulfonate, phytol toluenesulfonate, or **isophytol** in the presence of Sc[N(CF₃SO₂)₂]₃. II was refluxed with **isophytol** and Sc[N(CF₃SO₂)₂]₃ for 2.5 h in the dark to give 93% I.

ST alpha tocopherol prepn scandium complex catalyst; Friedel Crafts reaction methylhydroquinone **phytol** **isophytol**

IT Cyclocondensation reaction catalysts
Friedel-Crafts reaction catalysts

(prepn. of .alpha.-tocopherol with scandium complex as recyclable catalyst)

IT 144026-79-9, Scandium triflate

RL: **CAT (Catalyst use); USES (Uses)**

(prepn. of .alpha.-tocopherol with scandium complex as recyclable catalyst)

IT 10191-41-0P

RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)

(prepn. of .alpha.-tocopherol with scandium complex as recyclable catalyst)

IT 150-86-7, Phytol 505-32-8, Isophytol

700-13-0, Trimethylhydroquinone 10236-16-5, Phytyl acetate
202747-36-2 202747-37-3 202747-38-4 202747-39-5

RL: RCT (Reactant); RACT (Reactant or reagent)

(prepn. of .alpha.-tocopherol with scandium complex as recyclable catalyst)

L25 ANSWER 17 OF 23 HCPLUS COPYRIGHT 2003 ACS

AN 1997:591002 HCPLUS

DN 127:176579

TI Preparation of dl-.alpha.-tocopherol and its acetate via reaction of 2,3,5-trimethylhydroquinone with phytol or isophytol

IN Jaedicke, Hagen; Grafen, Paul; Laas, Harald

PA BASF A.-G., Germany

SO Ger. Offen., 5 pp.

CODEN: GWXXBX

DT Patent

LA German

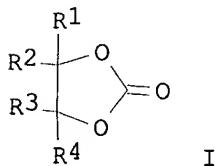
IC ICM C07D311-70

ICS C07D317-36

CC 30-20 (Terpenes and Terpenoids)

FAN.CNT 2

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|--|------------|----------|------------------|----------|
| PI | DE 19603142 | A1 | 19970731 | DE 1996-19603142 | 19960129 |
| | WO 9728151 | A1 | 19970807 | WO 1997-EP324 | 19970124 |
| | W: CN, JP, RU, SK, US | | | | |
| | RW: AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE | | | | |
| | EP 882036 | A1 | 19981209 | EP 1997-901601 | 19970124 |
| | R: CH, DE, FR, GB, LI | | | | |
| | CN 1211243 | A | 19990317 | CN 1997-191917 | 19970124 |
| | RU 2160258 | C2 | 20001210 | RU 1998-116519 | 19970124 |
| | JP 2002502360 | T2 | 20020122 | JP 1997-527279 | 19970124 |
| PRAI | DE 1996-19603142 | A | 19960129 | | |
| | DE 1996-19617444 | A | 19960502 | | |
| | WO 1997-EP324 | W | 19970124 | | |
| OS | MARPAT | 127:176579 | | | |
| GI | | | | | |



AB A procedure for the prepn. of dl-.alpha.-tocopherol and its acetate via acid-catalyzed reaction of 2,3,5-trimethylhydroquinone with phytol or isophytol in a soln. at elevated temp. and subsequent esterification of tocopherol with acetic anhydride is marked in that the

reaction takes place in a cyclic carbonate I [R1, R2, R3 = H, Me, Et; R4 = H, (un)substituted Ph, alkoxy] at 100 - 200.degree.. Thus, 2,3,5-trimethylhydroquinone in propylene carbonate contg. catalytic orthoboric and oxalic acids at 150.degree. is treated with a soln. of **isophytol** in heptane over 10 mins. to give 95% dl.-alpha.-tocopherol.

- ST tocopherol acetate prep; trimethylhydroquinone reaction **phytol**
isophytol
- IT 77-92-9, Citric acid, uses 87-69-4, (+)-L-Tartaric acid, uses
 109-63-7, Boron trifluoride etherate 144-62-7, Oxalic acid, uses
 10043-35-3, Orthoboric acid, uses
 RL: **CAT (Catalyst use); USES (Uses)**
 (prep. of .alpha.-tocopherol and its acetate via reaction of
 trimethylhydroquinone with **phytol** or **isophytol**)
- IT 96-49-1, Ethylene carbonate 108-32-7, Propylene carbonate 4437-69-8,
 Isobutylene carbonate 4437-85-8, 1,2-Butylene carbonate
 RL: NUU (Other use, unclassified); USES (Uses)
 (prep. of .alpha.-tocopherol and its acetate via reaction of
 trimethylhydroquinone with **phytol** or **isophytol**)
- IT 108-24-7, Acetic anhydride 150-86-7, **Phytol** 505-32-8,
Isophytol 700-13-0, 2,3,5-Trimethylhydroquinone
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (prep. of .alpha.-tocopherol and its acetate via reaction of
 trimethylhydroquinone with **phytol** or **isophytol**)
- IT 10191-41-0P, dl.-alpha.-Tocopherol
 RL: RCT (Reactant); **SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)**
 (prep. of .alpha.-tocopherol and its acetate via reaction of
 trimethylhydroquinone with **phytol** or **isophytol**)
- IT 52225-20-4P, dl.-alpha.-Tocopherol acetate
 RL: **SPN (Synthetic preparation); PREP (Preparation)**
 (prep. of .alpha.-tocopherol and its acetate via reaction of
 trimethylhydroquinone with **phytol** or **isophytol**)

- L25 ANSWER 18 OF 23 HCAPLUS COPYRIGHT 2003 ACS
 AN 1997:552632 HCAPLUS
 DN 127:149274
 TI Use of hydrogen bis(oxalato)borate as a condensation reaction catalyst
 IN Fuerbringer, Claude
 PA F. Hoffmann-La Roche Ag, Switz.
 SO Eur. Pat. Appl., 5 pp.
 CODEN: EPXXDW
 DT Patent
 LA French
 IC ICM C07B037-00
 ICS C07C041-48; C07C067-293; C07C403-10; C07D311-72
 CC 30-20 (Terpenes and Terpenoids)

FAN.CNT 2

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|---|------|----------|-----------------|----------|
| PI | EP 784042 | A1 | 19970716 | EP 1997-100109 | 19970107 |
| | R: AT, BE, CH, DE, DK, ES, FR, GB, IT, LI, NL | | | | |
| | CN 1161251 | A | 19971008 | CN 1997-102008 | 19970108 |
| | JP 09192493 | A2 | 19970729 | JP 1997-1788 | 19970109 |
| PRAI | CH 1996-96 | A | 19960112 | | |
| OS | CASREACT 127:149274 | | | | |
| AB | Hydrogen bis(oxalato)borate (I) is used as a catalyst in condensation reactions, such as Friedel-Crafts reactions, vinyl ether condensations, acylations, esp. in the prep. of dihydro-vitamin K1, d,l-alpha.-tocopherol and its acetate. Thus, trimethylhydroquinone is condensed with | | | | |

isophytol in presence of I to give 92% d,l-.alpha.-tocopherol, which is acetylated in 92% yield in presence of I.

ST hydrogen bisoxalatoborate prep condensation reaction catalyst; tocopherol prep hydrogen bisoxalatoborate catalyst

IT Condensation reaction catalysts
 (use of hydrogen bis(oxalato)borate as a condensation reaction catalyst)

IT 83145-82-8P
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)
 (use of hydrogen bis(oxalato)borate as a condensation reaction catalyst)

IT 144-62-7, Ethanedioic acid, reactions 505-32-8, Isophytol
 534-15-6, Acetaldehyde dimethylacetal 700-13-0,
 Trimethylhydroquinone 1303-86-2, Diboron trioxide, reactions 2211-28-1
 6068-62-8 7319-16-6, Methyl propenyl ether 16910-82-0
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (use of hydrogen bis(oxalato)borate as a condensation reaction catalyst)

IT 10191-41-0P, dl-.alpha.-Tocopherol
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
 (use of hydrogen bis(oxalato)borate as a condensation reaction catalyst)

IT 52225-20-4P, dl-.alpha.-Tocopherol acetate 98944-42-4P 103325-26-4P
 193347-01-2P 193347-05-6P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (use of hydrogen bis(oxalato)borate as a condensation reaction catalyst)

L25 ANSWER 19 OF 23 HCPLUS COPYRIGHT 2003 ACS
 AN 1997:533639 HCPLUS
 DN 127:190871
 TI Method of producing (.+.-)-tocopherol or (.+.-)-tocopheryl acetate
 IN Jaedicke, Hagen; Grafen, Paul; Laas, Harald
 PA Basf A.-G., Germany; Jaedicke, Hagen; Grafen, Paul; Laas, Harald
 SO PCT Int. Appl., 21 pp.
 CODEN: PIXXD2
 DT Patent
 LA German
 IC ICM C07D311-72
 CC 30-30 (Terpenes and Terpenoids)
 Section cross-reference(s): 45
 FAN.CNT 2

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|--|------|----------|------------------|----------|
| PI | WO 9728151 | A1 | 19970807 | WO 1997-EP324 | 19970124 |
| | W: CN, JP, RU, SK, US | | | | |
| | RW: AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE | | | | |
| | DE 19603142 | A1 | 19970731 | DE 1996-19603142 | 19960129 |
| | DE 19617444 | A1 | 19971106 | DE 1996-19617444 | 19960502 |
| | EP 882036 | A1 | 19981209 | EP 1997-901601 | 19970124 |
| | R: CH, DE, FR, GB, LI | | | | |
| | RU 2160258 | C2 | 20001210 | RU 1998-116519 | 19970124 |
| | JP 2002502360 | T2 | 20020122 | JP 1997-527279 | 19970124 |
| PRAI | DE 1996-19603142 | A | 19960129 | | |
| | DE 1996-19617444 | A | 19960502 | | |
| | WO 1997-EP324 | W | 19970124 | | |
| OS | CASREACT 127:190871 | | | | |
| AB | A method is disclosed of producing (.+.-)-.alpha.-tocopherol or | | | | |

(.+-.)-.alpha.-tocopheryl acetate by acid catalyzed reaction of 2,3,5-trimethylhydroquinone (TMH) with **phytol** or **isophytol** (IP) in a solvent at raised temp. and, where appropriate, subsequent esterification of the tocopherol thus obtained with acetic anhydride. The method is characterized in that the reaction is carried out in an optionally substituted cyclic five-ring carbonate such as 1,2-propylene carbonate, or in an optionally substituted five-ring lactone such as .gamma.-butyrolactone, as the solvent at temps. of between 50 and 200.degree.. The reaction works particularly well if, following the reaction of TMH and **phytol** or IP, the tocopherol which separates out as an upper phase as the reaction mixt. cools and/or the reaction mixt. is extd. using a suitable aliph. hydrocarbon, the tocopherol is isolated by distn. from the ext., and the sepd. cyclic carbonate or .gamma.-lactone which can contain excess TMH and acidic catalyst is reused as solvent. In many cases, it has been shown to be advantageous to carry out the reaction of TMH with **phytol** or IP with removal of the water as azeotrope, using a suitable hydrocarbon and/or in the presence of a mixt. of ortho-boric acid with oxalic acid, tartaric acid or citric acid, or alternatively in the presence of BF₃ etherate as the acidic catalyst. Surprisingly, the five-ring carbonates and five-ring lactones prove to have sufficient stability under the reaction conditions and suitable solvent characteristics to permit the process to be carried out continuously.

ST tocopherol acetate prep
 IT 77-92-9, Citric acid, uses 87-69-4, Tartaric acid, uses 144-62-7,
 Oxalic acid, uses 10043-35-3, Ortho-boric acid, uses
 RL: **CAT (Catalyst use); USES (Uses)**
 (method of producing (.+-.)-tocopherol or (.+-.)-tocopheryl acetate)
 IT 10191-41-0P, (.+-.)-.alpha.-Tocopherol 52225-20-4P,
 (.+-.)-.alpha.-Tocopheryl acetate
 RL: **IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)**
 (method of producing (.+-.)-tocopherol or (.+-.)-tocopheryl acetate)
 IT 96-48-0, .gamma.-Butyrolactone 108-32-7, 1,2-Propylene carbonate
 RL: **MSC (Miscellaneous)**
 (method of producing (.+-.)-tocopherol or (.+-.)-tocopheryl acetate)
 IT 150-86-7, **Phytol** 505-32-8, **Isophytol**
 700-13-0, 2,3,5-Trimethylhydroquinone
 RL: **RCT (Reactant); RACT (Reactant or reagent)**
 (method of producing (.+-.)-tocopherol or (.+-.)-tocopheryl acetate)

L25 ANSWER 20 OF 23 HCAPLUS COPYRIGHT 2003 ACS

AN 1997:496858 HCAPLUS

DN 127:109079

TI Process for the preparation of d,l-.alpha.-tocopherol in the presence of a perfluoroalkenesulfonic acid catalyst

IN Bonrath, Werner

PA F. Hoffmann-La Roche Ag, Switz.

SO Eur. Pat. Appl., 5 pp.

CODEN: EPXXDW

DT Patent

LA German

IC ICM C07D311-72

CC 30-20 (Terpenes and Terpenoids)

FAN.CNT 1

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|-------|----------|-----------------|----------|
| ----- | ----- | ----- | ----- | ----- |
| PI EP 782993 | A1 | 19970709 | EP 1996-120823 | 19961223 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, IT, LI, NL | | | | |
| JP 09194472 | A2 | 19970729 | JP 1996-346857 | 19961226 |

| | | | |
|------------------------|--|----------------|----------|
| CN 1160049 | A 19970924 | CN 1996-123196 | 19961227 |
| US 5900494 | A 19990504 | US 1997-778479 | 19970103 |
| PRAI CH 1996-31 | 19960105 | | |
| OS CASREACT 127:109079 | | | |
| AB | The title process involves reacting trimethylhydroquinone with isophytol in the presence of a polyperfluoroalkenesulfonic acid in an aprotic solvent between 80 and 140.degree.. Thus, a mixt. of trimethylhydroquinone and Nafion NR 50 in toluene was heated at 107.degree., isophytol was added over 2 h, and the resulting mixt. was refluxed for 30 min to give 75.33% (.+-.)-.alpha.-tocopherol. | | |
| ST | tocopherol prepn; methylhydroquinone condensation isophytol ; condensation trimethylhydroquinone isophytol | | |
| IT | Sulfonic acids, uses | | |
| | RL: CAT (Catalyst use) ; USES (Uses) (alkene, polyperfluoro; prepn. of .alpha.-tocopherol in presence of a perfluoroalkenesulfonic acid catalyst) | | |
| IT | Condensation reaction | | |
| | Condensation reaction catalysts | | |
| | Solvents (prepn. of .alpha.-tocopherol in presence of a perfluoroalkenesulfonic acid catalyst) | | |
| IT | 118473-68-0, Nafion NR 50 | | |
| | RL: CAT (Catalyst use) ; USES (Uses) (prepn. of .alpha.-tocopherol in presence of a perfluoroalkenesulfonic acid catalyst) | | |
| IT | 10191-41-0P, Ephanyl | | |
| | RL: IMF (Industrial manufacture) ; SPN (Synthetic preparation) ; PREP (Preparation) (prepn. of .alpha.-tocopherol in presence of a perfluoroalkenesulfonic acid catalyst) | | |
| IT | 60-29-7, Diethyl ether, uses 96-48-0, .gamma.-Butyrolactone 108-88-3, Toluene, uses 141-78-6, Ethyl acetate, uses | | |
| | RL: NUU (Other use, unclassified) ; USES (Uses) (prepn. of .alpha.-tocopherol in presence of a perfluoroalkenesulfonic acid catalyst) | | |
| IT | 505-32-8, Isophytol 700-13-0, Trimethylhydroquinone | | |
| | RL: RCT (Reactant) ; RACT (Reactant or reagent) (prepn. of .alpha.-tocopherol in presence of a perfluoroalkenesulfonic acid catalyst) | | |

L25 ANSWER 21 OF 23 HCAPLUS COPYRIGHT 2003 ACS

AN 1983:72494 HCAPLUS

DN 98:72494

TI .alpha.-Tocopherol

PA Kuraray Co., Ltd., Japan

SO Jpn. Tokkyo Koho, 2 pp.

CODEN: JAXXAD

DT Patent

LA Japanese

IC C07D311-72

CC 30-20 (Terpenes and Terpenoids)

FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|---|------|----------|-----------------|----------|
| PI | JP 57040150 | B4 | 19820825 | JP 1979-75511 | 19790614 |
| | JP 55027174 | A2 | 19800227 | | |
| PRAI | JP 1979-75511 | | 19790614 | | |
| AB | .alpha.-Tocopherol (I) was prep'd. by condensation of trimethylhydroquinone (II) with phytol halide in the presence of Sn. Thus, phytol chloride, prep'd. from 28.5 g isophytol , was added to a refluxing mixt. of | | | | |

12.17 g II, 1.0 g Sn, and 20 mL ligroin over 3 h, the mixt. refluxed for 3 h, 16.33 g Ac₂O and 3.27 g NaOAc were added, and the resulting mixt. was refluxed 2 h to give 38.5 g (.-+.-).alpha.-tocopherol acetate, which was hydrolyzed to I. Use of 4.5 g Fe instead of Sn gave only 20.16 g (.-+.-).alpha.-tocopherol acetate.

- ST alpha tocopherol; condensation trimethylhydroquinone isophytol chloride; tin catalyst condensation tocopherol
 IT Condensation reaction
 (of trimethylhydroquinone with phytol chloride in .alpha.-tocopherol prepn.)
 IT Condensation reaction catalysts
 (tin, for trimethylhydroquinone and phytol chloride, in tocopherol prepn.)
 IT 7440-31-5, uses and miscellaneous
 RL: CAT (Catalyst use); USES (Uses)
 (catalyst, for condensation of trimethylhydroquinone and phytol chloride, in tocopherol prepn.)
 IT 700-13-0
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (condensation of, with phytol chloride)
 IT 84416-26-2
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (condensation of, with trimethylhydroquinone in prepn. of .alpha.-tocopherol)
 IT 7695-91-2P 10191-41-0P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (prepn. of, from trimethylhydroquinone and phytol chloride)

L25 ANSWER 22 OF 23 HCAPLUS COPYRIGHT 2003 ACS

AN 1978:443854 HCAPLUS

DN 89:43854

TI dl-.alpha.-Tocopherol

IN Yoshino, Youziro; Kondo, Kazuko

PA Nisshin Flour Milling Co., Ltd., Japan

SO Ger. Offen., 10 pp.

CODEN: GWXXBX

DT Patent

LA German

IC C07D311-72

CC 30-30 (Terpenoids)

Section cross-reference(s): 27

FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|----|-------------|------|----------|-----------------|----------|
| PI | DE 2743920 | A1 | 19780330 | DE 1977-2743920 | 19770929 |
| | DE 2743920 | C2 | 19841018 | | |
| | JP 53044570 | A2 | 19780421 | JP 1976-115965 | 19760929 |
| | JP 60019309 | B4 | 19850515 | | |
| | US 4217285 | A | 19800812 | US 1979-11882 | 19790213 |

PRAI JP 1976-115965 19760929
 US 1977-837640 19770928
 AB DL-.alpha.-Tocopherol (I) was prep'd. with high purity by condensing trimethylhydroquinone (II) with phytol or isophytol in the presence of silicic acid-Al₂O₃ and/or silica gel, ZnCl₂, and a protonic acid. Thus, a mixt. of 25.0 g isophytol, 13.5 g II, 13.5 g silicic acid-Al₂O₃ or -silica gel, 6.0 g ZnCl₂, and 0.5 g 35% HCl was heated at 68.degree. for 4 h to give 99.8% I (95.8% purity).

ST alpha tocopherol

IT Silica gel, uses and miscellaneous

RL: CAT (Catalyst use); USES (Uses)

(catalyst from silicic acid, zinc chloride, acid, and, for condensation of trimethylhydroquinone with **phytol**)

IT 1343-98-2
 RL: **CAT (Catalyst use); USES (Uses)**
 (catalyst from aluminum oxide, zinc chloride, acid, and, for condensation of trimethylhydroquinone with **phytol**)

IT 7646-85-7, uses and miscellaneous
 RL: **CAT (Catalyst use); USES (Uses)**
 (catalysts from silicic acid, aluminum oxide, acid, and, for condensation of trimethylhydroquinone with **phytol**)

IT 7647-01-0, uses and miscellaneous 7664-38-2, uses and miscellaneous
 7664-93-9, uses and miscellaneous
 RL: **CAT (Catalyst use); USES (Uses)**
 (catalysts from silicic acid, aluminum oxide, zinc chloride and, for condensation of trimethylhydroquinone with **phytol**)

IT 53809-96-4, uses and miscellaneous
 RL: **CAT (Catalyst use); USES (Uses)**
 (catalysts from silicic acid, zinc chloride, acid, and, for condensation of trimethylhydroquinone with **phytol**)

IT 700-13-0
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (condensation of, with **phytol**)

IT 150-86-7 505-32-8
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (condensation of, with trimethylhydroquinone)

IT 10191-41-0P
 RL: **SPN (Synthetic preparation); PREP (Preparation)**
 (prepn. of, by condensation of trimethylhydroquinone with **phytol**)

L25 ANSWER 23 OF 23 HCAPLUS COPYRIGHT 2003 ACS
 AN 1975:16963 HCAPLUS
 DN 82:16963
 TI .alpha.-Tocopherol
 IN Omura, Yoshiaki; Nishida, Takashi; Tanomura, Masahisa; Tamai, Yoshin; Mori, Fumio; Hosogai, Takeo; Ninagawa, Yoichi; Itoi, Kazuo
 PA Kuraray Co., Ltd.
 SO Jpn. Kokai Tokkyo Koho, 3 pp.
 CODEN: JKXXAF
 DT Patent
 LA Japanese
 NCL 16E41
 CC 30-40 (Terpenoids)
 FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|----|-------------|------|----------|-----------------|----------|
| PI | JP 49070972 | A2 | 19740709 | JP 1972-114039 | 19721113 |
| | JP 57038588 | B4 | 19820816 | | |

PRAI JP 1972-114039 19721113
 AB .alpha.-Tocopherol (I) was prep'd. by condensing **isophytol** or **phytol** (II) with trimethylhydroquinone (III) in the presence of catalysts comprising Friedel-Craft catalyst, Zn (or Sn), and traces of acids. E.g., 29.65 g II was added to a mixt. of III 15.22, BF₃.Et₂O 14.19, Zn 1.31, and AcOH 1 g in hexane in 2 hr with reflux and the whole kept refluxed 2 hr with azeotropic removal of resultant H₂O to give 38.33 g dl-I.

ST tocopherol; **phytol** condensation trimethylhydroquinone catalyst; hydroquinone trimethyl condensation **phytol**; catalyst condensation **phytol** trimethylhydroquinone

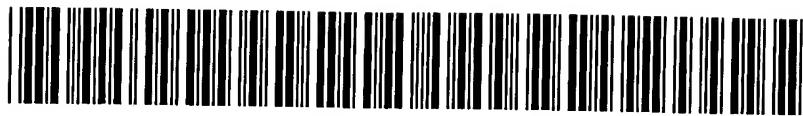
IT Condensation reaction catalysts

IT 109-63-7 (boron trifluoride, for **phytol** with trimethylhydroquinone)
RL: **CAT (Catalyst use); USES (Uses)**
(catalysts, for condensation of **phytol** with
trimethylhydroquinone)

IT 700-13-0
RL: **RCT (Reactant); RACT (Reactant or reagent)**
(condensation of, with **phytol**, catalysts for)

IT 150-86-7
RL: **RCT (Reactant); RACT (Reactant or reagent)**
(condensation of, with trimethylhydroquinone, catalysts for)

IT 10191-41-0P
RL: **SPN (Synthetic preparation); PREP (Preparation)**
(prepn. of)



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